VOLUMETRIC ANALYSIS

I. M. KOLTHOFF

Professor and Head
Division of Analytical Chemistry
University of Minnesota
Minneapolis, Minnesota

R. BELCHER

Reader in Analytical Chemistry
The University of Birmingham
Birmingham, England

with the cooperation of

V. A. STENGER

Analytical Research Chemist
The Dow Chemical Company
Midland, Michigan

G. MATSUYAMA

Senior Research Chemist
Research Department
Union Oil Company of California
Brea, California

VOLUME III

TITRATION METHODS:

Oxidation-Reduction Reactions

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PREFACE

This third and last volume of *Volumetric Analysis*, dealing with oxidation-reduction titrations, is long overdue. The senior author feels that an explanation for the lapse of time between the publication of the second and third volumes and also for the change in authorship is in order. After Volume II of this series was published, Dr. V. A. Stenger, the coauthor of the first two volumes, continued with the preparation of the third volume. After several years of interrupted progress it became apparent that lack of time would prevent him from finishing the book. With his usual thoroughness he prepared the manuscripts of the chapters dealing with titrations with permanganate and ceric cerium (Chapters II–IV). When no further progress was made, Dr. G. Matsuyama, at that time on the faculty of the University of Minnesota, was willing to become a collaborator. In a critical and systematic way he prepared the chapters dealing with iodometry (Chapters VI, VII, and IX–XI). A change of position made it impossible for him to continue his literary productivity. Dr. R. Belcher of the University of Birmingham (England) was then invited to cooperate in preparing most other chapters and to help in bringing up to date the chapters prepared by Drs. Stenger and Matsuyama. Dr. Belcher in turn enjoyed the valuable assistance of Dr. Alison M. G. Macdonald, also of the University of Birmingham.

With so many coworkers it becomes somewhat difficult to define the actual authorship of the book. The cooperation of Dr. Stenger and Dr. Matsuyama is acknowledged on the title page. The senior author wishes to express his gratitude to these ex-students of his and also to his coauthor, Dr. Belcher, who, with Dr. Macdonald, devoted much time and effort to drafting the remainder of the manuscript within a reasonable time.

Minneapolis, Minnesota I. M. KOLTHOFF
July, 1957

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CHAPTER I

REACTIONS, INDICATORS, AND GENERAL TECHNIQUES IN OXIDATION-REDUCTION TITRATIONS

In oxidation-reduction (redox) titrations the same general theoretical principles and techniques are often applied regardless of which standard oxidizing or reducing agent is used in the titration. In this section a brief discussion of some principles, indicators, reactions, and techniques of general application is presented in order to minimize undesirable repetition in the later chapters, which are concerned with particular standard oxidizing and reducing reagents.

Reactions Used in Redox Titrations. As has been discussed in Volume I, the equilibrium in a mixture of an oxidizing and reducing system can be calculated from the oxidation potentials of each redox couple. When the oxidation potential of a redox indicator in such systems is known, the sharpness of the color change at the end-point can be predicted.

When the activity of the oxidized or reduced form, or of both, of a redox couple is changed, the oxidation potential is affected. Drastic changes in activities can be brought about by addition of complex formers, by precipitation of one of the two forms of the couple, or by shaking out one of the forms in an immiscible, inert organic solvent. The last principle is scarcely ever used, although it could be applied, for example, to change the oxidation potential of the iodide-iodine system. The usual method of changing the oxidation potential of a given system is by complex formation. This principle is commonly applied to changing the oxidation potential of the ferric-ferrous system with, e.g., phosphoric acid, pyrophosphate, ethylene-diaminetetraacetic acid (EDTA) or fluoride which forms stable ferric complexes and either no, or less stable, complexes with ferrous iron. Thus the ferrous-ferric iron system becomes more strongly reducing in the presence of these complex formers. In the reaction

$$Fe^{3+} + I^- \rightleftharpoons Fe^{2+} + {}^1/_2 I_2$$

the addition of phosphoric or hydrofluoric acid prevents the process from going from left to right. In the presence of EDTA at the proper pH, the reaction goes quantitatively from right to left. The oxidation potential of the ceric-cerium system is greatly affected by the kind of anions present (see p. 122). Pyrophosphate stabilizes trivalent manganese, and manganese(II) is easily oxidized to the trivalent form in a pyrophosphate buffer. Many examples of the change of the oxidation potential of a system by complex formers are found in the practical part of the text.

A change of the oxidation potential by precipitation of one of the two forms of a redox couple is applied less frequently. One important application is made in the iodometric determination of cupric copper:

$$Cu^{2+} + I^- \rightleftharpoons Cu^+ + {}^1/_2 I_2 \tag{1}$$

$$\underline{Cu^+ + I^- \rightleftharpoons CuI} \tag{2}$$

$$Cu^{2+} + 2I^- \rightleftharpoons CuI + {}^1/_2 I_2 \tag{3}$$

Because of the insolubility of cuprous iodide, reaction (1) proceeds quantitatively to the right. On the other hand, in the presence of a compound which forms a strong complex with cupric copper (citrate, pyrophosphate, EDTA) reaction (1) can be made to proceed quantitatively from right to left. Another application of insolubility is often used in dealing with the ferri-ferrocyanide couple. Lead ferrocyanide is insoluble, but the ferricyanide is soluble. Thus the oxidation potential of the system is increased in the presence of lead. Zinc ferrocyanide is much less soluble than the ferricyanide, and again excess of zinc greatly increases the oxidation potential. This can be used in the iodometric determination of ferricyanide (p. 344) and of zinc (p. 345).

In practice, the problem often arises of determining one oxidizing (or reducing) agent in the presence of one or more other oxidizing (or reducing) substances. When the difference in oxidation potential of two oxidizing agents is sufficiently marked, there is usually no great difficulty in titrating one in the presence of the other. For example, in a mixture of permanganate or ceric cerium or chromic acid with ferric iron, the stronger oxidizing agent can be titrated with ferrous iron and the ferric iron does not interfere. The stronger oxidizing agents can also be titrated with a strong reducing agent, like chromous or titanous chloride; with a suitable indicator the first end-point is found when all stronger oxidant is reduced, while the iron is still in the ferric state. The ferric iron is then reduced and a second end-point is obtained with another indicator. When the oxidation potentials of the two oxidizing (or reducing) substances which are present do not differ enough to allow a selective titration of one in the presence of the other, the principles presented earlier in this section can sometimes be applied. For example, in a mixture of permanganate and ceric cerium it should be possible to make use of the fact that the ceric cerium forms stable complexes with pyrophosphate in the pH range between 1 and 7. In such a medium, permanganate is a much stronger oxidizing agent than ceric cerium and it should be possible to titrate the permanganate with ferrous iron (to Mn(III)) before the cerium(IV) is reduced.

If the oxidation potentials of two oxidizing (or reducing) substances in a solution do not differ much and cannot be made to differ much by applying the above principle, a separation may be in order. The principles on which separations are based are discussed in some general textbooks on quantitative analysis.[1] Chemical separations often involve precipitation methods which are rarely used in redox titrations. Of course, precipitation *per se* is of importance and is frequently applied, e.g., in the determination of appropriate cations as oxalates, iodates, periodates, chromates, or as chelates (8-hydroxyquinoline, etc.) by titration of the excess of precipitant in the supernatant liquid or filtrate or by titration of the precipitate. Electroseparations are often carried out at a constant potential at a mercury cathode or more commonly with suitable reductors (see p. 9).

Among the methods of separation involving physical processes, distillation can often be used to advantage, not only in organic but also in inorganic analysis. For example, arsenic can be separated from many other constituents by distillation as $AsCl_3$ (followed by the titration of arsenic(III) in the distillate) (p. 514). The interference of ammonia in bromometric reactions in alkaline medium can be avoided by removing ammonia by distillation. The interference of iron in the iodometric determination of the active oxygen in pyrolusite can be eliminated by heating with hydrochloric or hydrobromic acid and collecting the chlorine or bromine in potassium iodide solution (p. 284). In this connection, reference may be made to the work of Conway, who developed simple techniques for distillation of micro quantities. His general procedure is described on p. 31.

Immiscible solvent extraction is another technique which can be of oxidize manganese(II) to permanganate. They precipitated the excess of periodate and the iodate formed from the reaction of periodate with manganese as the mercuric salts, and determined the permanganate in the filtrate.

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[1] See, e.g., I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, 3rd ed., Macmillan, New York, 1953, p. 72.

Silver peroxide has been used to oxidize vanadium(IV) to vanadate, manganese(II) to permanganate, chromium(III) to chromate,[5] and cerous to ceric.[6] The excess of oxidant is filtered off. This reagent is said to be superior to sodium bismuthate.

Perchloric acid is now used extensively as an oxidizing agent and finds particular application in metallurgical analysis for the determination of chromium and vanadium. Oxidation by perchloric acid only takes place with the hot concentrated solution; accordingly, rapid cooling and dilution eliminates the oxidizing properties of perchloric acid and it is then possible to titrate chromate with ferrous sulfate in the presence of cold dilute acid which is unreactive.

TABLE I

Oxidizing agent	Removal of excess
Potassium permanganate	Conversion to MnO_2 by boiling with manganous sulfate; MnO_2 removed by filtration. Warming with $NaNO_2$ or NaN_3
Ammonium persulfate (Usually with Ag^+)	Destroyed by boiling
Ozone	Boiling
Hydrogen peroxide	Boiling; sometimes with catalyst present
Potassium periodate	Precipitation as $Hg_5(IO_6)_2$
Lead dioxide	Filtering
Sodium bismuthate	Filtering
Potassium chlorate	Boiling in acid solution
Perchloric acid	Dilution and cooling

After oxidation with perchloric acid the solution must be cooled rapidly to room temperature by immersing in a slurry of ice. If this precaution is not taken, some slight reduction of chromate takes place owing to its reacting with hydrogen peroxide which is formed as a reduction product of hot concentrated perchloric acid.[7]

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[5] M. Tanaka, *Bull. Chem. Soc. Japan*, **26**, 299 (1953); **27**, 10 (1954); cf. J. J. Lingane and D. G. Davis, *Anal. Chim. Acta*, **15**, 201 (1956), who have recently recommended the use of argentic oxide for the oxidation of manganese(II), chromium(III), and cerium(III).

[6] K. Kimura and Y. Murakimi, *Mikrochemie*, **36/37**, 727 (1951).

[7] G. F. Smith, *Analyst*, **80**, 16 (1955); cf. *Perchloric Acid*, 4th ed., G. F. Smith Chem. Co., Columbus, Ohio, 1946.

When the solution is cool it is diluted with water, reboiled for a few minutes to expel chlorine, and is then recooled and titrated.

The more important oxidizing agents and the methods used to remove excess of oxidant are listed in Table I.

Reduction of Higher Valency States. In volumetric analysis a constituent is often reduced to a definite valence form which then can be titrated with a standard solution of an oxidizing agent. The extent to which the reduction takes place can be calculated from the oxidation potentials of the two systems under consideration, as has been discussed in Volume I. Quite generally such a reduction can be accomplished by electrolysis at a mercury cathode at a controlled cathode potential. Advantages of the mercury cathode are: it has a high hydrogen overvoltage making it possible to get quantitative reduction in acid medium without interference by hydrogen evolution; no foreign reagent is introduced into the system; and it is often possible in a mixture of two oxidizing agents to reduce only one constituent at a selected potential while the other is not affected.[8] When an oxidizing agent can be reduced to different valence forms, it is often possible to obtain quantitatively only one of the valence forms dependent upon the potential of the mercury during the electrolysis.

The mercury cathode needs special equipment, and simpler procedures with other reducing agents are often preferred. Of course, the excess of reducing agent used must be removed from the solution before the reduced constituent is titrated. The removal can be accomplished by boiling when the reducing agent is volatile, like hydrogen sulfide and sulfur dioxide. However, these reducing agents are not used to the same extent as others (cf. p. 11). More common is the use of stannous chloride, the excess of which can be removed by oxidation with mercuric chloride (see p. 10). If the procedure is carried out properly, the mercurous chloride does not interfere in the subsequent titration.

For obvious reasons, metal and metal amalgam reductors have, in general, great advantages over other reducing agents, and they are frequently used in volumetric analysis. When dealing with a base metal, like zinc, which gives hydrogen evolution even in weakly acid medium, it is advantageous to cover the metal with a layer of amalgam. Because of the high hydrogen overvoltage at the amalgam, little of the reductor is wasted by hydrogen evolution and its life period is extended. Several workers prefer to carry out the reductions with a liquid amalgam instead of with metal in the granulated state. The oxidation potential of the amalgam is slightly greater (less strongly reducing) than that of the bulk metal (unless the amalgam is saturated) and varies with the activity of the metal in the amalgam. For example, the e.m.f. of the cell, Cd_xHg_{100-x} (x is mole per cent)/$CdSO_4$ solution/Cd, is 0.073 v. when $x = 1.75$, 0.051 v. when $x = 15.2$, and 0.0007 v. when $x = 93$. A thallium amalgam electrode with 3.25 per cent thallium has a potential which is 0.11 v. more positive than that of pure thallium in the same medium. For our purpose the potential of very dilute metal amalgams is only of academic interest, because in volumetric work relatively concentrated amalgams are used. As a fair approximation we may consider the potential of such an amalgam to be of the order of 50 mv. less negative than that of the bulk metal in the same medium. When the amalgam is saturated with metal, the standard potentials are −0.76 v. for zinc, −0.40 v. for cadmium, −0.13 v. for lead, and +0.32 v. for bismuth.

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[8] See, e.g., J. J. Lingane, *Electroanalytical Chemistry*, Interscience, New York-London, 1953.

The potential of a metal electrode is given by:

$$E = E_0 + (RT/nF) \log [\mathrm{M}^{n+}]$$

the activity of the metal being constant. It is readily seen that the reducing action of a metal can be increased greatly when the solution contains an excess of a constituent which forms a slightly soluble compound, or a stable complex, or a slightly dissociated compound, with the metal ions. When the metal forms a precipitate and the excess of anion is so large that we can consider it constant, the potential of the metal electrode also becomes constant. Consider the silver reductor in $1N$ hydrochloric acid. Taking the solubility product of silver chloride equal to 10^{-10}, we find for the potential of the reductor:

$$E = 0.798 + 0.06 \log 10^{-10} = 0.198 \text{ v.}$$

0.798 being the standard potential of silver. The silver reductor has been used for the quantitative reduction of ferric iron and other metals (p. 15). A much stronger silver reductor is obtained when silver is placed in a solution of potassium argentocyanide in an excess of cyanide. For example, the potential of a silver electrode in a solution which is $0.05M$ in argentocyanide and $1M$ in potassium cyanide is −0.56 v. (vs. NHE) as compared to +0.2 v. in $1N$ hydrochloric acid. Thus a fairly noble metal like silver can be made to behave as a base metal such as cadmium or zinc, dependent on the silver-ion concentration in the half cell. Of course, the constituent which is used to keep the silver-ion concentration small should not interfere with the titration after the reduction. For example, silver in iodide would be much stronger reducing than silver in chloride, but iodide would interfere badly in titrations with such oxidizing agents as permanganate, ceric cerium, and dichromate.

Mercury as a reductor is very similar to silver. A mercury electrode in $1N$ hydrochloric acid has about the same potential as silver in the same medium.

By the use of different metal and amalgam reductors selective reductions can be made (see pp. 12 and 19). The reducing power of the metal depends on its place in the electrolytic voltage table. Thus zinc reduces more strongly than cadmium, which is a stronger reducing agent than lead; bismuth is still weaker. A pentavalent vanadium solution is reduced by zinc to divalent vanadium but is reduced by bismuth amalgam only to the tetravalent state. If vanadium is to be determined in the presence of iron, the latter is reduced to the divalent form by both reductors. Thus a differential titration can be carried out.

Metals are used in various forms for reduction; as sheet, powder, or shot, as powder or granules in a reductor column, or as liquid amalgams. This type of reduction will be dealt with more fully in the next section.

Hydrogen sulfide: Hydrogen sulfide is sometimes used for the reduction of iron(III) to iron(II) and has some advantages. Recently[9] it has regained some of its former popularity for reducing iron to the ferrous state because of its selectivity. Copper is precipitated as sulfide and may be filtered off, and vanadium(V) is reduced to vanadium(IV), which does not interfere in the subsequent titration provided that dichromate is used. Molybdenum is not completely precipitated because a small amount may be reduced to a valency state which does not yield an insoluble sulfide. When it is present the precipitated sulfide is filtered off, hydrogen sulfide is boiled out of the filtrate, a few drops of permanganate are added to reoxidize the reduced molybdenum, and hydrogen sulfide is then repassed. Platinum sulfide may precipitate if platinum ware has been used in the opening-out treatment of minerals.

[9] British Standard 1121: Pt. 33, 1955, "Methods for Analysis of Iron and Steel: Iron in Ores, Slags and Refractories."

Procedure. Heat the solution (which should be about 200 ml. in volume and about 1*N* in sulfuric acid) to boiling and saturate with hydrogen sulfide. Remove from the source of heat and continue to pass hydrogen sulfide for 10–15 minutes. Boil off the hydrogen sulfide (usually until the solution is reduced to about one third of its original bulk). Test for completeness of removal with lead acetate paper. Rinse down the sides of the flask and boil for a few minutes longer. Cool rapidly to room temperature and titrate, preferably with dichromate (p. 177).

Notes: (1) Hydrogen sulfide should be passed through a water bubbler to trap iron salts contained in the spray from the generator.

(2) If sulfides are precipitated, they should be filtered off as soon as the solution is cool and washed with 1:50 sulfuric acid saturated with hydrogen sulfide. If molybdenum is present, the last traces should be removed by adding a few drops of dilute permanganate to the filtrate and repeating the reduction.

(3) Kessler[10] preferred to remove the last traces of sulfide by precipitation with mercuric chloride as basic mercury sulfochloride.

Sulfur dioxide: Sulfur dioxide or sulfurous acid is also used for the reduction to ferrous iron. The excess is removed by boiling and by passing carbon dioxide. Care must be taken with regard to the adjustment of the acidity; as this increases, so does the time of reduction and above 1*N* the reaction does not go to completion. At an acidity of 5*N*, sulfurous acid oxidizes ferrous iron. An acidity of 0.1*N* in sulfuric acid is about the maximum concentration which should be used, but if thiocyanate ions are present a higher limit can be tolerated (p. 187).

Procedure: To the test solution containing not more than 0.2 g. of iron, add 2*N* ammonia solution until a permanent precipitate is obtained. Add sulfuric acid (1:9) dropwise and shake the container well after each addition until the precipitate dissolves. Dilute to about 200 ml. with water. Add 25 ml. of a freshly prepared saturated solution of sulfur dioxide, heat to boiling, and continue to boil for about 15 minutes. Add some calcite and continue to boil until all the sulfur dioxide is expelled. Cool rapidly and titrate.

Note: Titanium(IV) and chromium(III) are unaffected by this treatment. Vanadium(V) is reduced to vanadium(IV).

Stannous chloride: In hot solution, ferric iron is rapidly reduced by stannous chloride; the excess is destroyed by the addition of mercuric chloride:

$$Sn^{2+} + 2HgCl_2 \longrightarrow Sn^{4+} + Hg_2Cl_2 + 2Cl^-$$

Small amounts of mercurous chloride are not appreciably affected by the oxidants normally used for the titration of ferrous iron.

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[10] F. Kessler, *Z. anal. Chem.*, **11**, 249 (1872).

It is important to avoid the addition of more than a slight excess of stannous chloride; otherwise the following reaction takes place:

$$Sn^{2+} + HgCl_2 \longrightarrow Sn^{4+} + Hg + 2Cl^-$$

Finely divided mercury, which is black or grey in color, then reacts with the titrant. A large excess of mercurous chloride (produced by an excessive addition of stannous chloride) also reacts to some extent with the titrant.

The titration should be completed as quickly as possible because of possible interaction between mercurous chloride and iron(III). According to Meineke,[11] the following reaction occurs:

$$Hg_2Cl_2 + 2FeCl_3 \longrightarrow 2HgCl_2 + 2FeCl_2$$

When permanganate is used as titrant it is necessary to add preventive solution to overcome the effect of chloride ions (p. 77). If ceric sulfate is preferred, an indicator other than ferroin should be used because it is not altogether satisfactory when mercurous chloride is present. The end-point has a pink tinge because of adsorption of the dye by the precipitate.

The procedure is described in detail on p. 84; cf. p. 187.

Reductor columns: One of the most popular and convenient methods of effecting reduction to a desired valency state is to pass the test solution through a column of a suitable granulated metal or amalgam packed into a glass tube.

Jones Reductor: The first column of this type was described by Jones,[12] who used zinc for effecting reduction; his apparatus is known as the Jones reductor. More efficient reduction is obtained with amalgamated zinc, and it is in this form that the zinc is now generally used.[13] Stone and Hume[14] have discussed the use of amalgamated zinc for reduction and state that the rate of reaction between the zinc amalgam and the substance which is being reduced depends chiefly on the nature of the latter and on the concentration of zinc at the surface of the amalgam.

The degree of amalgamation should be adjusted where possible to conform with the nature of the reducible substance. With iron(III) and cerium(IV), which are reduced by mercury as well as zinc, a 1 per cent mercury content is suitable; at high acid concentrations it may be desirable to have 5 per cent of mercury present. With metals which do not react with mercury, only sufficient mercury to control the evolution of hydrogen should be present (0.1–1.0 per cent); otherwise the rate of reaction is retarded.

---

[11] C. Meineke, *Z. öffentl. Chem.*, 4, 433 (1898).

[12] C. Jones, *Trans. Am. Inst. Min. Engrs.*, 17, 411 (1888–89).

[13] P. W. Shimer, *J. Am. Chem. Soc.*, 21, 723 (1899).

[14] H. W. Stone and D. N. Hume, *Ind. Eng. Chem., Anal. Ed.*, 11, 598 (1939).

It has been claimed that hydrogen peroxide may be formed intermediately in the column when air is present and might pass through the column and be titrated with permanganate.[15] Burdick[16] passed oxygen through the reductor and found hydrogen peroxide in the effluent when the zinc amalgam was moistened only with water; in the presence of acid, hydrogen peroxide could not be detected. Lundell and Knowles[17] found that, when hydrogen peroxide in sulfuric acid solution was passed through a Jones reductor, the hydrogen peroxide was completely destroyed. However, the presence of air in the reductor should be avoided because it usually causes low results. This can readily be achieved when necessary by sweeping dissolved air out of solutions with carbon dioxide.

Some later investigators[18] are still insistent that hydrogen peroxide formation occurs, especially with the silver reductor, and hydrogen peroxide has actually been found in the effluent. The effect was overcome by saturating the acid solutions with carbon dioxide. It should be noted, however, that in these cases very small amounts of iron were being determined.

The ions shown in Table II are reduced to a definite valency stage in the Jones reductor. Their behavior in the silver reductor is included for comparison. Compounds of several other elements are re-

TABLE II

Reduction in the Jones and Silver Reductors

Jones reductor, sulfuric acid medium	Silver reductor, hydrochloric acid medium
$Cr^{3+} \rightarrow Cr^{2+}$	Cr^{3+} not reduced
$Cu^{2+} \rightarrow Cu^{0}$	$Cu^{2+} \rightarrow Cu^{+}$ (2*M* HCl)
$Eu^{3+} \rightarrow Eu^{2+}$	
$Fe^{3+} \rightarrow Fe^{2+}$	$Fe^{3+} \rightarrow Fe^{2+}$
$Mo^{6+} \rightarrow Mo^{3+}$	$Mo^{6+} \rightarrow Mo^{5+}$ (2*M* HCl)
$Ti^{4+} \rightarrow Ti^{3+}$	Ti^{4+} not reduced
$UO_2^{2+} \rightarrow U^{4+}$ and U^{3+}	$UO_2^{2+} \rightarrow U^{4+}$
$V^{5+} \rightarrow V^{2+}$	$V^{5+} \rightarrow V^{4+}$

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[15] M. Traube, *Ber.*, **26**, 1471 (1893).

[16] W. L. Burdick, *J. Am. Chem. Soc.*, **48**, 1179 (1926).

[17] G. E. F. Lundell and H. B. Knowles, *Ind. Eng. Chem.*, **16**, 724 (1924).

[18] C. F. Fryling and F. V. Tooley, *J. Am. Chem. Soc.*, **58**, 826 (1936). Cf. C. C. Miller and R. A. Chalmers, *Analyst*, **77**, 2 (1952).

duced to the elements, e.g., nickel, platinum, gold, arsenic, antimony. Tungsten, rhenium, and columbium are reduced to less definite valency stages, but with columbium a reasonably satisfactory determination has been based on this reduction (p. 95).

Uranium is partially reduced to uranium(III) in the zinc reductor; air is bubbled through the solution, after it has passed through the reductor, for a few minutes at room temperature to oxidize uranium(III) to uranium(IV). Quadrivalent uranium is quite stable under these conditions and is then titrated in this state.

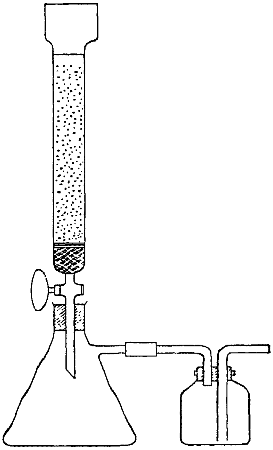

FIG. 1. Jones reductor.

A suitable form of the Jones reductor is shown in Fig. 1. It consists of a glass tube 18–20 mm. in diameter and 35–55 cm. in length. Into this is packed a 25–45 cm. column of amalgamated zinc, which is supported on a porcelain filter disk covered with a mat of asbestos or glass wool. The latter should be packed sufficiently tightly to hold all particles of zinc. Below the support the tube is fitted with a stopcock to control the flow of solution. The end of the tube passes through a rubber stopper into a filter flask of suitable capacity (usually 500 ml.). The side-arm of the flask is connected via a trap to suction which is regulated by means of a screw clamp.

The zinc particles should be 20–30 mesh and free from impurities, such as iron and organic matter; they are amalgamated with 0.1–5.0 per cent of mercury. The degree of amalgamation is governed by the nature of the substances to be reduced, the acidity of the solution, the length of the reductor column, and the speed of flow to be used.

Preparation of the Zinc Amalgam: To a suitable quantity of 20 mesh zinc add sufficient 1*N* hydrochloric acid to cover it and pour off after 1 minute. Add the appropriate amount of 0.25*M* mercuric nitrate or chloride and stir vigorously for 3–5 minutes. Decant the solution from the zinc and wash with water twice or thrice by decantation. Fill the reductor tube with water, then add the zinc in portions until the tube is filled to the required height. Wash with about 500 ml. of water and keep the zinc covered with water to prevent the formation of basic salts which tend to clog the column.

Procedure for Use of the Jones Reductor. Wash the reductor five or six times with 30 ml. portions of 1:20 sulfuric acid and discard the washings. Attach the receiver and pass the test solution (100–150 ml.), which may be 0.5–5*N* in either hydrochloric or sulfuric acid, through the column at a rate of 75–100 ml. per minute. When the test solution is about 1 cm. above the zinc column, wash with three 25 ml. portions of 1:20 sulfuric acid and finally with three 25–35 ml. portions of water. At no time during these operations should the level of the liquid be allowed to fall below 1 cm. above the surface of the zinc. Allow the last portion of wash liquid to flow through under gravity, wash the end of the delivery tube, and titrate the contents of the flask. Take care to see that the top of the zinc column is covered with water and place an inverted beaker over the funnel top of the reductor until it is required again.

Carry out a blank determination.

Notes: (1) When a reductor column has not been in use for some little time it is necessary to wash it well with dilute sulfuric acid before the test solution is poured through, otherwise high results are obtained. In normal circumstances it is sufficient to wash first with 25–50 ml. of dilute acid.

(2) Ammoniacal solutions react with mercury and should never be passed through the column. Compounds of copper, nickel, and other metals which are reduced to the elements should be removed. Platinum, in small amounts derived from platinum vessels, is rapidly reduced to the metal on the upper part of the column and does not interfere.

(3) Nitric acid and nitrates interfere because they are reduced to hydroxylamine and other compounds; they should be removed by heating the solution to fumes of sulfuric acid twice or thrice.

(4) Organic matter should be destroyed by attack with sulfuric and nitric acids. Care should be taken in the final operation to expel all traces of nitric acid.

(5) Apart from iron(II) and uranium(IV), the reduced solutions are unstable and should be protected from atmospheric oxidation by an inert gas or by being caught in a solution of ferric sulfate. The latter is reduced to the more stable ferrous sulfate, which can then be dealt with in the usual way.

Silver Reductor: Reduction by silver powder was first recommended by Hoenig,[19] and rotating cylinders of silver sheet were tried by Gooch and Scott.[20] This method never achieved much popularity until Walden and his coworkers[21] demonstrated that a reductor column containing silver had some advantages for certain operations over the well-established Jones reductor. (See Table II for a comparison of the two reductors.)

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[19] A. Hoenig, *Z. anal. Chem.*, **54**, 441 (1915); cf. G. Edgar, *J. Am. Chem. Soc.*, **38**, 1297 (1916); G. Edgar and A. R. Kemp, *ibid.*, **40**, 777 (1918); N. A. Tananaeff, *Z. anorg. u. allgem. Chem.*, **136**, 193 (1924).

The following elements have been determined: iron,[22] copper,[23] uranium,[23] molybdenum,[24] and vanadium.[25] A hydrochloric acid medium is always used.

The acidity is more critical than with the Jones reductor. In $2M$ hydrochloric acid, molybdenum is reduced to the pentavalent form, whereas in $4M$ hydrochloric acid it is reduced to the trivalent form. In the Jones reductor the trivalent form is obtained over a wide range of acid concentrations.

Later investigators[18] have shown that hydrogen peroxide is formed and interferes seriously with the determination of small amounts of iron. Fryling and Tooley[18] overcome this by saturating the solution with hydrogen; Miller and Chalmers[18,26] used carbon dioxide.

Preparation of the Silver Reductor: Dissolve 30 g. of silver nitrate in 400 ml. of water, add a few drops of nitric acid, suspend a sheet of electrolytic copper 10 cm. square in the solution, and stir vigorously until the silver has been completely precipitated. Wash by decantation with dilute sulfuric acid until free from most of the copper. Transfer to the reductor tube (of design similar to the Jones reductor but shorter since a 12 cm. column of metal is adequate) with water, agitate to remove air pockets, and wash with dilute sulfuric acid until completely free from copper. Fill the column with $1M$ hydrochloric acid until required for use.

The column becomes coated and discolored with silver chloride after continued use. When this extends down the column to three quarters the length, fill the column with $0.1M$ sulfuric acid and place a zinc rod in contact with the column until reduction is complete. The use of the reductor is described on pp. 150, 153, and 156.

Notes: (1) Smith and Cagle[27] recommended a coarser size of silver powder prepared by electrodeposition. Columns prepared in this way required more frequent generation. This was achieved by simply washing the column with dilute ammonia solution.

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[20] F. A. Gooch and W. Scott, *Am. J. Science*, 46, 1135 (1918).

[21] G. H. Walden, L. P. Hammett, and S. M. Edmonds, *J. Am. Chem. Soc.*, **56**, 57 (1934).

[22] *Idem, ibid.*, 350.

[23] N. Birnbaum and S. M. Edmonds, *Ind. Eng. Chem., Anal. Ed.*, 12, 155 (1940).

[24] N. Birnbaum and G. H. Walden, *J. Am. Chem. Soc.*, **60**, 64 (1938).

[25] J. J. Lingane and L. Meites, *J. Am. Chem. Soc.*, 69, 277 (1947).

[26] Cf. A. F. Colson, *Analyst*, 70, 1255 (1945); I. C. Wells, *Anal. Chem.*, 23, 511 (1951).

[27] G. F. Smith and F. W. Cagle, *Anal. Chem.*, 20, 183 (1948).

(2) Huffman[28] considered the zinc-sulfuric acid reduction method for regeneration to be too lengthy. He allowed a chromous chloride solution to percolate slowly through the column until blue chromous ions were observed in the effluent. The column was then washed well with dilute sulfuric acid. The time for regeneration, including preparation of the chromous chloride (reduction of chromic chloride with zinc and hydrochloric acid) occupied only 20–30 minutes whereas Huffman found a time of 48 hours was necessary by the zinc rod method.

(3) Miller and Chalmers[18] recommended the use of gold crucibles in place of platinum when opening out silicates. Platinum(IV) carried through from the fusion was reduced to platinum(II) and slowly reacted with ceric sulfate to give fading end-points. Hillebrand *et al.*,[29] however, state that platinum salts are reduced to the metal and form a silver-platinum couple which has more powerful reducing properties than silver alone; unwanted reductions can then occur such as that of titanium(IV) to titanium(III).

Lead Reductor: Treadwell[30] also recommended the lead reductor, and in more recent times some application has been found for this method of reduction in the determination of uranium. The main difficulty in its use is the formation of lead sulfate films when sulfuric acid is present. Cooke *et al.*[31] found that when the hydrochloric acid concentration is maintained above 2.5N the film formation is prevented. They used this reductor for the determination of uranium (p. 190). The advantages claimed for the lead reductor are: (1) lead can be obtained in a state of high purity, thus eliminating the need for blank determinations; (2) since hydrogen is not evolved, amalgamation is not necessary; (3) the reductor need not be freed from air, for its presence does not introduce errors.

It should be noted, however, that, as with the Jones and silver reductors, conflicting statements are made in the literature concerning the formation of hydrogen peroxide. Sill and Peterson[32] state that hydrogen peroxide is formed in the lead reductor (and in the Jones reductor). They emphasize that air bubbles must be removed to prevent its formation.

Preparation of Lead Reductor: Cover a suitable quantity of granulated C.P. lead with hydrochloric acid (1:9) containing about 0.1 per cent of iron and set aside overnight. Decant off the solution and transfer the lead to a column about 25 cm. long and 2 cm. in diameter. Wash with six 25 ml. portions of 1:15 hydrochloric acid before use.

[28] E. H. Huffman, *Ind. Eng. Chem., Anal. Ed.*, 18, 278 (1946).

[29] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, *Applied Inorganic Analysis*, Wiley, New York, 1953, p. 113.

[30] W. D. Treadwell, *Helv. Chim. Acta*, 5, 732 (1922).

[31] W. D. Cooke, F. Hazel, and W. M. McNabb, *Anal. Chem.*, 22, 654 (1950).

[32] C. W. Sill and H. E. Peterson, *Anal. Chem.*, 24, 1175 (1952).

Notes: (1) Unless a trace of ferric salt is added to the lead the first determination is slightly low.

(2) Sill and Peterson[32] used 20–100 mesh granulated lead which was packed into a column 1 cm. diameter and 30 cm. long. A 1 cm. length of glass wool was packed at the bottom and top of the column. When not in use the reductor was covered with water. These investigators also comment on the limitations of the Jones reductor.

Determination of Iron with the Lead Reductor:[33] Dilute the solution to about 50 ml.; the acidity at this stage should be approximately $2N$ in sulfuric acid. Pour through the column at a rate of 50–75 ml. per minute and wash with three to four 25 ml. portions of water containing 5–10 ml. of hydrochloric acid per liter. Take care to keep the liquid level above the surface of the lead. Titrate the reduced solution immediately with ceric sulfate or dichromate.

Notes: (1) Some lead chloride may precipitate but does not interfere with the titration.

(2) After use, rinse the reductor with 200 ml. of boiling, dilute hydrochloric acid (1:99).

(3) For other applications see pp. 157 and 190.

Other Metal Reductor Columns: Cadmium has been recommended in place of zinc.[34] It is said to have some advantages, but this statement is to be doubted; at least the zinc reductor is much more widely used. Treadwell[34] described methods using the cadmium reductor for the determination of several metals. A cadmium amalgam was used by Helger.[35] He claimed that only slight hydrogen evolution occurred and the amalgam did not coalesce like the conventional zinc amalgam.

Lobunets[36] used the cadmium reductor for the determination of several organic nitro compounds. The amines produced were determined by the Day-Taggart bromination method (p. 536).

Other reductor columns which have been used are bismuth (for molybdenum and vanadium),[37] antimony (for iron, tin, uranium, and tungsten),[38] nickel (for iron, molybdenum, tin, titanium, uranium, vanadium, and tungsten),[38] copper (for iron, vanadium, and molybdenum),[39] tin (for iron, molybdenum, and uranium)[40] and iron (for titanium and uranium).[41]

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[33] Cf. H. H. Willard and H. Diehl, *Advanced Quantitative Analysis*, Van Nostrand, New York, 1943.

[34] W. D. Treadwell, *Helv. Chim. Acta*, **4**, 551 (1921); **5**, 732 (1922); cf. A. Claassen and J. Visser, *Rec. trav. chim.*, **60**, 213 (1941); W. I. Stephen, *Ind. Chemist*, **28**, 13, 55, 107 (1952) (general review of metal reductors).

[35] B. Helger, *Svensk Kem. Tidskr.*, **61**, 62 (1949).

[36] M. M. Lobunets, *Zav. Lab.*, **7**, 872 (1938).

[37] E. V. Ankudimova, *Chem. Abstr.*, **49**, 12187 (1955).

[38] C. Yoshimura, *J. Chem. Soc. Japan*, **76**, 409 (1955).

[39] *Idem., ibid.*, **73**, 702 (1952).

[40] *Idem., ibid.*, **74**, 116 (1953).

[41] *Idem., ibid.*, **74**, 544 (1953).

Reduction with Amalgams: Several Japanese investigators have used various kinds of liquid amalgam in titrimetric analysis. Nakazono[42] used liquid zinc amalgam and claimed the following advantages: (1) complete reduction is achieved in a few minutes; (2) no correction is required as in the Jones reductor; (3) very reliable results are obtained; (4) the amalgam can be used repeatedly.

Kikuchi[43] used zinc amalgam for the determination of iodic, bromic, and chloric acids as well as methylene blue. Kano[44] used cadmium amalgam before the electrometric titration of iron, molybdenum, uranium, vanadium, and titanium. Hakomori[45] determined phosphoric acid by reduction of phosphomolybdic acid.

Kikuchi[46] and Kano[47] applied amalgams to the differential titration of titanium, of uranium and iron, and of titanium and iron. Systematic studies on this interesting subject have been carried out by Someya[48] to whose work we shall later refer briefly. The reduction of various metals with liquid amalgams is discussed more fully on pp. 90 to 95.

The use of liquid amalgams is still being studied extensively, and the following references indicate the scope of this work.[49] Bismuth amalgam has been used for reduction of iron and uranium,[50] zinc amalgam for iron, molybdenum, uranium, and antimony,[51] and cadmium amalgam for tungsten and iron.[52]

Yoshimura[53] studied the behavior of nitrate with zinc and bismuth amalgams but obtained inaccurate results owing to nitrite formation. He recommended that urea be added to react with the nitrite. He was able to determine iron, vanadium, tin, and uranium in this way without the need for first removing nitrate.

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[42] T. Nakazono, *J. Chem. Soc. Japan*, **42**, 526, 761 (1921); *Chem. Abstr.*, **16**, 1543 (1922).

[43] S. Kikuchi, *J. Chem. Soc. Japan*, **43**, 173 (1922); *Chem. Abstr.* **16**, 1716 (1922).

[44] N. Kano, *J. Chem. Soc. Japan*, **43**, 333 (1922); *Chem. Abstr.*, **16**, 2818 (1922).

[45] S. Hakomori, *J. Chem. Soc. Japan*, **43**, 734 (1922); *Chem. Abstr.*, **17**, 1930 (1923).

[46] S. Kikuchi, *J. Chem. Soc. Japan*, **43**, 544 (1922); *Chem. Abstr.*, **17**, 247 (1923).

[47] N. Kano, *J. Chem. Soc. Japan*, **44**, 37, 47 (1923); *Chem. Abstr.*, **17**, 2842 (1923).

[48] K. Someya, *Sci. Repts. Imp. Univ. Tôhoku*, **14**, 48, 235 (1925); **15**, 399, 417, 421 (1926); *Z. anorg. u. allgem. Chem.*, **138**, 291 (1924); **148**, 58 (1925); **152**, 368 (1926); cf. I. Tananaev and E. Dawitaschvili, *Z. anal. Chem.*, **107**, 175 (1936).

[49] For a comprehensive account of the use of liquid amalgams see the papers by W. I. Stephen, *Ind. Chemist*, **29**, 31, 79, 128, 169 (1953).

[50] C. Yoshimura, *J. Chem. Soc. Japan*, **75**, 603 (1954).

[51] *Idem, ibid.*, **74**, 116 (1953); **76**, 411 (1955); cf. T. Nittar, *ibid.*, **73**, 885 (1952) (vanadium).

[52] S. Ishimaru and K. Saito, *ibid.*, **54**, 305 (1951).

[53] C. Yoshimura, *ibid.*, **74**, 448 (1953).

The behavior of several amalgams and mercury with various ions is summarized in Table III (cf. p. 12). The original papers should be consulted for details of all these procedures.

TABLE III

Reducing Action of Liquid Amalgams and Mercury[a]

	Valency stage after reduction by:					
Element	Zn amalgam	Cd amalgam	Bi amalgam	Pb amalgam	Sn amalgam	Hg
Iron	2	2	2	2	2	2
Titanium	3	3	3	3	3	—
Vanadium	2	2	4	2	2	4
Uranium	3, 4[b]	4	4	4	—	4
Molybdenum	3	3	3, 5[b]	3	3	5
Tungsten	3	3, 4[b]	3	3	3	—
Tin	—	—	2	—	2	—
Copper	—	—	1	—	1, 0[b]	—
Chromium	2	—	—	2	—	—
Arsenic	—	—	—	—	3, 0[b]	—
Antimony	—	—	—	—	3, 0[b]	3

[a] A dash in the table does not necessarily mean that reduction does not take place; but the presence of data signifies that the reduction has been applied to the determination of the substance concerned.

[b] Both valency states produced; in some cases dependent on acidity.

Preparation of Amalgams. Zinc Amalgam: Heat about 3 g. of pure zinc (granulated or in sticks) on a water bath with about 100 g. of mercury and a little dilute sulfuric acid. Wash the amalgam carefully with water and separate it from all floating solid material in a separatory funnel. Store the amalgam under dilute sulfuric acid; it can then be used repeatedly and kept for a long time. Save the solid conglomerate of zinc and mercury which remains in the funnel for further use; add it to the consumed amalgam when the zinc content of the latter becomes too small.

Cadmium Amalgam: Prepare in exactly the same way as zinc amalgam.

Lead Amalgam: Clean pure lead rods from the surface coating of lead chloride with a little concentrated hydrochloric acid. Add the rods to mercury and heat until a homogeneous liquid is obtained. Cool, wash with water, and separate the liquid from the solid phase as above.

According to Someya,[48] lead amalgam is much more versatile than zinc amalgam; it reacts only slowly with dilute sulfuric or hydrochloric acid and can remain in contact with these acids for an unlimited time without noticeable decrease in its reducing power.

Bismuth Amalgam: Prepare in the same way as zinc amalgam, but use hydrochloric acid instead of sulfuric acid.

Reduction Apparatus after Someya (Fig. 2): *A* is the inlet funnel with cock *a;* the funnel has a capacity of about 10 ml. *B* is a large separatory funnel of capacity 150–200 ml. A gas inlet tube leads to the cock *b*. The small vessel *C* of capacity 15–20 ml. is attached to funnel *B* with rubber tubing *E* which can be opened and closed by the clip *e*.

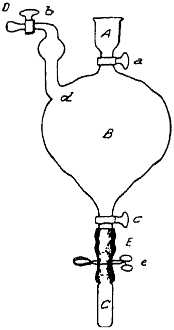

FIG. 2. Reduction apparatus after Someya.

Reduction Procedure: Fill vessel *C* and rubber tubing *E* with freshly boiled out water or hydrochloric acid, so that about 1 ml. of water rises into funnel *B*. Close tap *c* and clip *e* whenever the air bubbles have been completely driven up from *E* and *C* by compression of the tubing. Place 100–200 g. of amalgam in funnel *B* through inlet *A* and add the test solution. If necessary, replace the air in *B* by carbon dioxide through *b* and *d*. Close the taps and shake the mixture carefully. The characteristic color of the solution allows the completion of the reaction to be observed. Transfer the amalgam to the small vessel *C* by opening tap *c* and by pressing the rubber tubing. The water in *C* rises and simultaneously washes the amalgam; thus the amalgam can be separated without loss of the test solution. Titrate the solution in *B* through inlet *A*. If the solution is sensitive to atmospheric oxidation, introduce an atmosphere of carbon dioxide through *b*. Partial solution of carbon dioxide in the liquid produces a slight vacuum so that the titrant can easily be added through *a*. If necessary, the titrant can be forced into the vessel by slight pressure with the hand on the inlet tube. If necessary, the whole system can be carefully heated over a gas flame.

Note: When the reduced form of the metal is fairly stable in air (e.g., iron(II)), it is often sufficient to shake 50 ml. of the solution (4*N* in sulfuric acid) for a few minutes with 30–50 ml. of the amalgam in a wide-mouthed stoppered bottle. The reduced solution is then decanted from the amalgam into the titration flask and the amalgam is washed 2 or 3 times with boiled out distilled water.

Smith and Kurtz[54] reduced ions which did not require an inert atmosphere in a 500 ml. conical flask. When reduction was complete, 30–50 ml. of carbon tetrachloride or chloroform was added; three layers were thus formed with the reduced solution separated from the amalgam by the organic solvent. The uppermost layer could be stirred and titrated without disturbing the lower layers. When an inert atmosphere was necessary, a modified form of the flask was used (Fig. 3) which allowed an inert gas to flow over the surface. Various types of amalgam were used for the reduction.

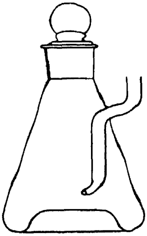

FIG. 3. Modified form of Smith and Kurtz reduction flask.[54]

Procedure (for iron): To 25 ml. of the solution about 0.1*N* in sulfuric acid contained in the flask add 20 ml. of lead amalgam and 100 ml. of 1:6 sulfuric acid. Stopper the flask and shake vigorously for 2 minutes. Rinse down the sides of the flask, add 35 ml. of carbon tetrachloride, insert the stirrer into the uppermost layer, and titrate with ceric sulfate.

Note: The results were slightly low; hence the use of carbon dioxide to prevent reoxidation is advocated.

Reduction with Metals.

Zinc: Metallic zinc is one of the earliest known reducing materials;

$$Zn + 2Fe^{3+} \longrightarrow Zn^{2+} + 2Fe^{2+}$$

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[54] G. F. Smith and L. T. Kurtz, *Ind. Eng. Chem., Anal. Ed.,* 14, 854 (1954).

it was used even in 1846 by Margueritte.[55] It must be completely free from soluble materials which reduce permanganate and especially free from iron. It should be tested with permanganate after dissolution in sulfuric acid and if necessary, a correction should be made. Skrabal[56] found that the zinc must also be tested for the presence of substances which do not bleach permanganate alone but may do so in the presence of iron. This test is done by adding to the filtered zinc solution 45 ml. of 0.1N ferrous sulfate solution and titrating with permanganate; the titer should be the same as that of the pure iron solution. Chemically pure zinc dissolves slowly and the reduction is only complete after several hours; it is therefore better to heat the system. To the strongly acid solution, which must not contain nitric acid, are added an abundant amount of zinc and, if possible, some platinum foil or gauze (to form a galvanic element). The mixture is heated while carbon dioxide passes slowly through the flask or, more simply, a Bunsen or a Contat-Göckel trap is placed on the flask.

The ferric solution is heated until reduction is complete, cooled, and then filtered (if any zinc, or a small residue, such as carbon, remains) through glass wool or asbestos. Air oxidation of ferrous solution is now insignificant for such solutions are fairly stable in the cold.

Other Metals: *Aluminum* is sometimes used, but care should be taken to ensure that it is free from iron. It has been used in the determination of various elements.[57] Simon *et al.*[58] used *nickel shot* for the differential reduction of iron and tin. In the cold only iron is reduced. After titrating iron(II), tin (IV) is reduced by heating and is finally titrated iodometrically.

Finely divided copper has been used[59] for the reduction of iron(III); the solution is shaken with the copper powder for a few minutes and the latter is then filtered off.

Several metallic ions are reduced by *elemental mercury* (cf. p. 19). The reducing action of mercury, like that of silver, is greatly increased by anions (chloride, etc.) which form slightly soluble or slightly dissociated mercury salts (cf. p. 8). Furman and Murray[60] reduced molybdenum by shaking with mercury; molybdenum(V) is formed (cf. p. 153). McKay *et al.*[61]

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[55] F. Margueritte, *Ann. Chim. Phys.*, (3) 18, 244 (1846).

[56] A. Skrabal, *Z. anorg. Chem.*, **42**, 1 (1904); *Z. anal. Chem.*, 42, 359 (1903).

[57] Cf. E. R. Riegel and R. D. Schwartz, *Anal. Chem.*, **24**, 1803 (1952); **26**, 410 (1954).

[58] A. C. Simon, P. S. Miller, J. C. Edwards, and F. B. Clardy, *Anal. Chem.*, 18, 496 (1946).

[59] K. Kurschner and K. Schaner, *Z. anal. Chem.*, **68**, 1 (1936); cf. J. O. Percival, *Ind. Eng. Chem., Anal. Ed.*, **13**, 71 (1941).

[60] N. H. Furman and W. M. Murray, *J. Am. Chem. Soc.*, 58, 429, 1689, 1843 (1936).

[61] L. W. McKay and W. T. Anderson, *J. Am. Chem. Soc.*, **43**, 2372 (1921); **44**, 1018 (1922); L. W. McKay, *Ind. Eng. Chem., Anal. Ed.*, **5**, 1 (1933).

had previously determined iron, antimony, and vanadium after reducing in this way. Uranium may also be determined.[62] Reference has already been made to the use of cadmium metal by Treadwell.[34,63]

Woods metal has been used as a reductant by several investigators.[64] When the test solution is boiled the alloy liquefies. As soon as the reduction is complete a platinum wire is inserted in the metal, which resolidifies on cooling and can be lifted out of the vessel. Uranium(III) and uranium(IV), iron(II), tungsten(III), titanium(III), and vanadium(II) are the final products of reduction, but with the last two metals the reaction does not appear to go to completion. Chlorate, bromate, and iodate are reduced to the corresponding halides and may be determined as such by Volhard's method.

Redox Resins: The use of redox or electron exchange resins was first suggested by Cassidy.[65] These may be defined as polymeric substances capable of taking part in reversible oxidation-reduction reactions.

Cassidy demonstrated that such polymeric substances could be prepared, his first product being polymerized vinyl hydroquinone. This was not completely successful; it was not possible to oxidize all the groups present and some loss of activity occurred when the resin was reduced and reoxidized. In a later publication,[66] it was shown that this partial failure was due to the low molecular weight of the vinyl hydroquinone polymer which corresponded mainly to dimer and trimer, thus giving different oxidizabilities. The presence of the hydroquinone group in the monomer inhibited the chain-propagating reaction. When the hydroxyl groups of vinyl hydroquinone were protected by preparing the diacetate or the dibenzoate, high polymer was readily obtained. The protecting groups were removed by saponification after polymerization.

By this process have been prepared polyvinyl hydroquinone and copolymers of vinyl hydroquinone and styrene, α-methylstyrene, 4-vinylpyridine, and a copolymer of vinylhydroquinone and styrene crosslinked by divinylbenzene. Molecular weights were found to be of the order of 69,000.

The resins reduced iodine and were themselves oxidized; after elution they liberated iodine from iodide solutions. As yet, these resins have not been applied analytically and more research is needed before they could be used safely for titrimetric analysis. The principle on which they are based is interesting; it should be possible to regenerate resins into their original states. Their apparent oxidation potential varies with pH. No extraneous material would be introduced into a solution which has been treated with a redox resin.

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[62] E. R. Caley and L. B. Rogers, *J. Am. Chem. Soc.*, 68, 2202 (1946).

[63] Cf. L. Mázor and L. Erdey, *Acta Chim. Acad. Sci. Hung.*, 2, 331 (1952).

[64] S. Kaneko and C. Nemoto, *J. Soc. Chem. Ind., Japan.* 35, 185 (1932); cf. P. G. Popov, *Ukrain. Khim. Zhur.*, 10, 428 (1935); G. F. Smith and C. S. Wilcox, *Ind. Eng. Chem., Anal. Ed.*, 9, 419 (1937); C. Yoshimura, *J. Chem. Soc. Japan*, 74, 325 (1953) (also Rose's metal).

[65] H. G. Cassidy, *J. Am. Chem. Soc.*, 71, 402 (1949).

[66] M. Ezrin and H. G. Cassidy, *Ann. N. Y. Acad. Sci.*, 57, 79 (1954).

The work is obviously in its infancy but appears to be of high promise and worthy of extensive investigation. So far, little attempt appears to have been made to extend this interesting new technique.[67]

REDOX INDICATORS (see Vol. I, p. 105)

The most useful indicators for titrations with strong oxidizing agents belong to the *o*-phenanthroline-ferrous group. The properties of this type of indicator are discussed on pp. 124 and 173, and their applications in Chapters IV and V. Many indicators of the diphenylamine type are also very useful, and their characteristics are described on pp. 123 and 170, and their application in Chapters III, IV, V, and XIV.

In the present general chapter the properties of some redox indicators which find less frequent application are discussed. For a more exhaustive treatment the reader is referred to the treatises of Tomíček[68] and Brennecke.[69]

Whitehead and Wills[70] have compiled a useful review of redox indicators, and they include a comprehensive table of all those which have been examined but have been found unsuitable for various reasons. The reviews by Kolthoff,[71] Gray,[72] and Nutten[73] should also be seen.

Triarylmethane Dyes. For most purposes potassium permanganate can be used as titrant without the need for indicator addition. In some cases, however, it is advantageous to use a suitable redox indicator, e.g., in titrations with dilute solutions ($0.01N$), in artificial light, or in the presence of highly colored ions. Many of the conventional redox indicators can be used for this purpose, e.g., diphenylaminesulfonic acid (p. 172), *N*-phenylanthranilic acid (p. 126), or ferroin (p. 124). Knop[74] made a systematic study of triarylmethane dyestuffs and found 25 which were suitable for titrations with permanganate. He finally selected 12 of these as being the most satisfactory; these are listed in Table IV.

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[67] See, however, J. E. Salmon and H. R. Tietze, *J. Chem. Soc.*, **1952**, 2324; H. Kakihana and K. Katou, *J. Chem. Soc. Japan*, **76**, 499 (1955).

[68] O. Tomíček, *Chemical Indicators*, Butterworths, London, 1951.

[69] E. Brennecke and E. Blasius, in G. Jander, ed., *Neuere Massanalytische Methoden*, F. Enke, Stuttgart, 1956, p. 251.

[70] T. H. Whitehead and C. C. Wills, *Chem. Revs.*, **29**, 69 (1941).

[71] I. M. Kolthoff, *Anal. Chem.*, **22**, 65 (1950).

[72] A. G. Gray, *J. Chem. Educ.*, **16**, 373 (1939).

[73] A. J. Nutten, *Metallurgia*, **42**, 271, 407 (1950).

TABLE IV

Triarylmethane Dyes of Knop

Indicator	Color of indicator: Neutral	Acid	Acid-oxidized form	*C.I.* No.
Acronol brilliant blue	Blue	Yellow-green	Yellow-red	664
Cyanine B	Blue	Yellow	Orange	713
Cyanol fast green 2G	Blue-green	Yellow	Pink	—[a]
Erioglaucine A	Blue	Green	Rose	671
Eriogreen B (G)	Blue-green	Yellow	Orange	735
Patent blue A	Blue	Yellow-green	Pink	714
Setocyanine supra	Blue	Yellow-green	Yellow-red	—[a]
Setoglaucine O	Blue	Yellow-green	Yellow-red	658
Setopaline conc.	Blue	Yellow	Orange	—[a]
Xylene blue AS	Blue	Yellow-green	Pink	673
Xylene blue VS	Blue	Yellow	Pink	672
Xylene cyanol FF	Blue	Yellow	Pink	715

[a] These dyestuffs are not listed in the *Colour Index.*

Stock solutions: 0.1 per cent in water.

Sensitivity: The addition of 0.1–0.2 ml. of 0.01*N* permanganate to 100 ml. of 1–5*N* sulfuric acid causes the color change.

The potential at which the color change occurs is between +0.6 and 0.7 v. against the normal calomel electrode or about 0.95 v. against the normal hydrogen electrode.[74] All the indicators are reversible. The indicator corrections are negligibly small in titrations with 0.1*N* permanganate.

It should be noted that complications arise in the titration of ferrous iron with permanganate in hydrochloric acid medium. In addition to the induced oxidation of the dyes, the effect of traces of chlorine is noticeable and is not eliminated by the addition of Zimmermann-Reinhardt solution. The result is that most of the indicator present is destroyed before the end-point is reached. The best results are obtained in hydrochloric acid medium with setoglaucine as indicator; it is particularly suitable for use after reduction of iron with stannous chloride, for the titration of iron on the micro scale, or when nickel or cobalt is present.

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[74] J. Knop, *Z. anal. Chem.* 77, 111 (1929); 85, 253 (1931); cf. J. Knop and O Kubelkova, *ibid.*, 77, 125 (1929); 85, 401 (1931); 100, 161 (1935).

Some of these indicators do not revert to the original color when back-titrated. Setoglaucine, for instance, changes to a blue-green instead of yellow; the sharpness is then somewhat enhanced.

A few of these indicators have been applied in titrations with ceric sulfate and have been found satisfactory for this purpose (p. 123). They are not suitable for titration with dichromate.

Erioglaucine and eriogreen are excellent indicators in the titration of ferrocyanide with permanganate in a sulfuric acid medium; the correction is negligible with $0.1N$ solutions. In a hydrochloric acid medium eriogreen is suitable, but a significant correction is necessary (0.1–0.15 ml. of $0.05N$ permanganate).

Several other dyestuffs have been recommended for permanganate and ceric sulfate titrations, but do not seem to have any advantage over those considered already. It is probable that the same dyestuff has been recommended as new more than once owing to the many alternative names which are available for the commercial products (cf. p. 124). In cases where dyestuffs are recommended, the Colour Index Number or the Schultz Number should always be given when available.

Diphenylamine Derivatives (cf. pp. 171–174): Oldfield and Bockris[75] determined the redox potential of several derivatives of diphenylamine over the range pH 0–2. Their results are summarized in Table V, the potentials being determined in 50 per cent acetone. The practical applications of these amines were not examined.

Erdey and Bodor[76] have since recommended indicator (3) (variamine blue) for various redox titrations particularly with ascorbic acid (p. 627), for iodometry (p. 212), or for vanadium-ferrous titration.[77] They state that the redox potential is 0.69 at pH 0 and 0.38 at pH 6, but the conditions of determination differed from those of Oldfield and Bockris.

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[75] L. F. Oldfield and J. O. M. Bockris, *J. Phys. & Colloid Chem.*, 55, 1255 (1951).

[76] L. Erdey and A. Bodor, *Z. anal. Chem.*, 137, 410 (1953).

[77] L. Erdey, K. Vigh, and E. Bodor, *Acta Chim. Acad. Sci. Hung.*, 7, 293 (1955)

Lederer and Ward[78] examined the redox properties of *o*-, *m*-, and *p*-tolylanthranilic acids. Only the ortho compound had suitable indicator properties. The color of the oxidized form of the meta compound was very unstable, and the para compound did not yield any color on oxidation. *o*-Tolylanthranilic acid gave a stable purple color when oxidized; the color change was reversible. The oxidation potentials of the ortho and meta compounds were 1.01 and 0.85 v. respectively.

TABLE V

Indicator	Color of oxidized form	E^0 (volts)
(1) 4-Aminodiphenylamine	Dark blue	0.76
(2) 4,4′-Diaminodiphenylamine	Dark blue	0.75
(3) 4-Amino-4′-methoxydiphenylamine	Violet	0.74
(4) 4-Amino-3-methoxydiphenylamine	Blue	0.64

Fluorescent and Chemiluminescent Indicators: Some fluorescent redox indicators have been described. They may be used with various titrants, e.g., permanganate, iodine, bromate.[79] The original papers should be consulted for details.

Chemiluminescent indicators have been recommended for certain redox titrations. Siloxene was proposed by Kenny and Kurtz (p. 127). They also used luminol for acid-base titrations.[80] Erdey and Buzás[81] have since recommended luminol (p. 577) and lucigenin (p. 650) as indicators for redox titrations in alkaline solution with hydrogen peroxide, sodium hypochlorite, and other titrants. The titrations were done in a dark chamber which enclosed the titration vessel; magnetic stirring was used.

Manometric Detection of the End-Point: Gottlieb[82] has described a new method for detecting the end-point in various types of titration. He uses an enclosed burette system with a manometer attached, and the end-point is detected by a change in pressure. For example, iron(II) and tin(II) are titrated with dichromate in the presence of hydrazine sulfate. At the end-point hydrazine begins to decompose and the released nitrogen exerts a pressure in the system. The original papers should be consulted for details.

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[78] M. Lederer and F. L. Ward, *Anal. Chim. Acta*, **6**, 1 (1952).

[79] H. Gotô and Y. Kakita, *J. Chem. Soc. Japan*, **63**, 120 (1942); **64**, 515 (1943); cf. O. Tomíček and V. Suk, *Chem. Listy*, **46**, 139 (1952).

[80] F. Kenny and R. B. Kurtz, *Anal. Chem.*, **23**, 339 (1951).

[81] L. Erdey and I. Buzás, *Acta Chim. Acad. Sci. Hung.*, **6**, 77, 93, 115, 123, 127 (1955).

[82] O. R. Gottlieb, *Anal. Chim. Acta*, **13**, 101, 214, 531 (1955); **14**, 24 (1956).

GENERAL APPARATUS

For Titrations with Air-Sensitive Solutions. Various devices have been described to avoid the risk of atmospheric oxidation of air-sensitive solutions after heating operations. One of the simplest is that known as the Contat-Göckel trap[83] (Fig. 4). The trap is filled with sufficient water or sodium bicarbonate solution to cover the end of the siphon tube. At the end of the heating period the trap is half filled with saturated sodium bicarbonate solution which is drawn into the flask as it cools. Carbon dioxide is liberated, and excess passes out through the trap. As the pressure inside the flask continues to fall, more sodium bicarbonate is drawn in and the process is repeated. Hence throughout the cooling period an atmosphere of carbon dioxide is maintained in the flask .

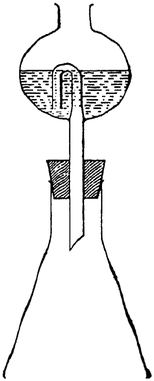

FIG. 4. Contat-Göckel trap.

Of course, an inert gas (nitrogen or carbon dioxide) may be passed through the solution if preferred. When solid sodium bicarbonate or solid carbon dioxide is used, only small portions should be added at a time and care must be taken to avoid losses due to spattering.

To avoid risk of oxidation during a titration the titration flask should be fitted with a three-holed stopper. The burette tip passes through one hole, and a delivery tube (which dips below the level of the solution) to pass inert gas through another hole; the third hole serves as an outlet for the inert gas.

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[83] A. Contat, *Chem. Ztg.* 22, 298 (1898); H. Göckel, *Z. angew. Chem.*, **13**, 620 (1899); cf. W. H. Jackson, *Analyst*, **78**, 443 (1953).

Bromine Flasks. Various types of flasks known as bromine flasks have been described. Their purpose is to prevent losses of bromine during the waiting periods. The flask due to Schulek and Clauder[84] is illustrated in Fig. 5 and was designed for the bromometric determination of oxine. Sufficient potassium iodide solution is placed in the cup to cover the stopcock (which is not greased); acid and other additions are made through the funnel. The use of this flask is described in more detail on p. 550.

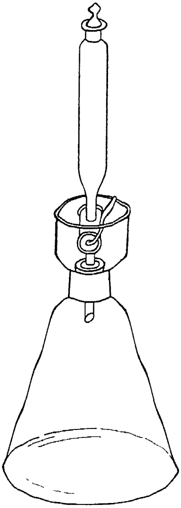

FIG. 5. "Bromine" flask of Schulek and Clauder.[84]

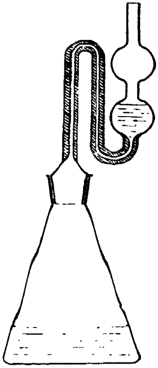

FIG. 6. "Bromine" flask of Erichsen and Rudolphi.

The flask shown in Fig. 6 was recommended by Erichsen and Rudolphi (p. 540) for the bromometric determination of phenols. The flask is 300 ml. in capacity and the capillary is of 2–3 mm. bore. Potassium iodide solution is placed in the bulb as shown, and at the end of the bromination period a small amount of air is sucked out of the flask through the bulbs and the iodide solution then flows into the flask. Further details of its use are given on p. 541.

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[84] E. Schulek and O. Clauder, *Z. anal. Chem.*, 108, 385 (1937).

Iodine Flasks. Some workers prefer to use a special flask for iodometric reactions to avoid risk of losses of iodine. This is shown in Fig. 7 and is known as an iodine flask. The solution to be analyzed is transferred to the flask and is treated with potassium iodide. The flask is stoppered and a solution of potassium iodide is placed in the cup to act as a seal during the time the reaction proceeds.

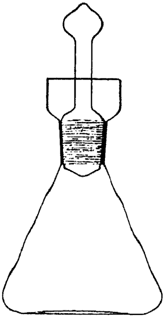

FIG. 7. Iodine flask.

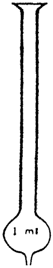

FIG. 8. Titration thief.

At the end of the reaction period the stopper is loosened so that the potassium iodide in the cup flows into the flask. The cup, the stopper, and the sides of the flask are then rinsed with water and the titration is carried out.

Avoiding Overtitration. When the amount of standard solution likely to be consumed in a titration is completely unknown, and an indicator is being used which gives no warning of the approach of the end-point, it is advisable to withdraw a small portion of the test solution and to titrate fairly rapidly until the indicator change takes place. This small portion of test solution is then reintroduced into the main solution. The indicator color will revert and the titration may then be completed more cautiously. Various devices have been suggested to facilitate this withdrawal. For example, a titration flask fitted with a small side-tube near the neck of the flask may be used. A small portion of the test solution may be introduced into this tube by tilting the flask. Probably the most simple and convenient method is to use the device known as a titration thief (Fig. 8). This has a bulb approximately 1 ml. in volume and the orifice is drawn out to about 2 mm. in diameter. It may readily be constructed from tubing 6–8 mm. in diameter. The tube is placed in the test solution and part of it enters the bulb. After the end-point has been reached the tube is lifted so that the test solution flows out. It is rinsed either by lifting it in and out of the solution twice or thrice, or by washing the inside with a fine jet from a wash bottle. The titration is then completed.

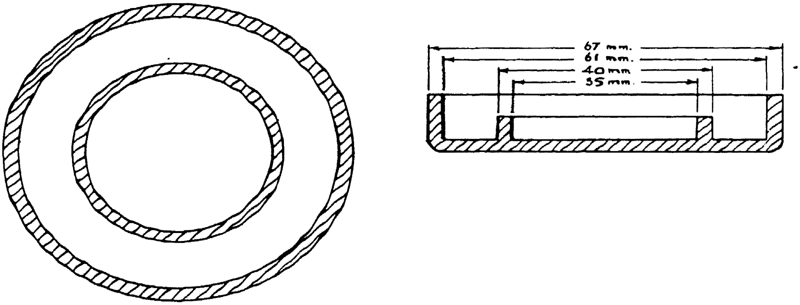

FIG. 9. Conway gas diffusion cell.[85]

Distillation. Sometimes it is necessary to distil a volatile product in order to separate it from interfering substances. Possibly the most common example of this is given by Bunsen's method for the iodometric determination of manganese dioxide. This is described more fully on p. 284. Ammonia may be removed by distilling in the apparatus shown on p. 168 of Volume II.

For work on the micro scale, Conway[85] has described special diffusion methods. The apparatus is essentially a 65 mm. Petri dish to which is sealed an inner, concentric, cylindrical chamber slightly shorter than the outer wall of the Petri dish so that the gas phase over the two chambers can mix when the cell is sealed with a glass plate. A sketch of the cell is shown in Fig. 9. The substance to be analyzed is placed in the outer compartment and is reacted with a suitable reagent so that a volatile product is formed. This is absorbed in a suitable reagent placed in the inner compartment and titrated. For example, bromide is treated with sulfuric acid-dichromate and the liberated bromine diffuses into potassium iodide solution. An equivalent amount of iodine is released and is titrated with thiosulfate. For successful application of this technique, it is necessary to follow the experimental details with considerable care. The original work should be consulted for these details.

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[85] E. J. Conway, *Microdiffusion Analysis and Volumetric Error*, Crosby-Lockwood, London, 1947.

CHAPTER II

POTASSIUM PERMANGANATE AS A VOLUMETRIC REAGENT

1. Oxidation States of Manganese. When potassium permanganate is used for titration in acid solution, the reaction may be expressed by the equation

$$\mathrm{MnO_4^-} + 8\mathrm{H}^+ + 5e \rightleftharpoons \mathrm{Mn}^{2+} + 4\mathrm{H_2O}$$

from which it is evident that the oxidation potential of a permanganate-manganous system is influenced greatly by the hydrogen-ion concentration (see Vol. I, p. 76):

$$E = E_0 - \frac{0.0591}{5} \log \frac{[\mathrm{Mn}^{2+}]}{[\mathrm{MnO_4^-}][\mathrm{H}^{+}}$$

The effect of manganous-ion concentration upon the potential is not given accurately by the above expression, however, since manganous ions are themselves capable of reducing permanganate with formation of trivalent manganic ions and manganese dioxide. In acid solution these reactions take place slowly, but with sufficient speed to cause gradual fading of the permanganate color after completion of a titration. The studies of Holluta[1] demonstrated that the mechanism of permanganate oxidation is complicated. Generally, titrations are carried out in acid solution, since they are then more likely to proceed directly to the end-point. On the other hand, some substances are oxidized more easily in neutral or alkaline solution. Here it is necessary to consider not only the oxidation potential of permanganate, but also the reducing action of the compound which is to be determined. Hydrazine, for example, is smoothly oxidized to nitrogen and water in alkaline medium, whereas in acid solution various other products are formed (p. 68). Sulfite, sulfide, and thiosulfate may be converted quantitatively to sulfate in the presence of alkali but are only partially oxidized if the solution is acid.

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[1] J. Holluta, *Z. physik. Chem.*, **101**, 34 (1922); **102**, 32, 276 (1922); **106**, 276, 324 (1923); **107**, 249, 333 (1923); **113**, 464 (1924); **115**, 137 (1925); J. Holluta and N. Weiser, *ibid.*, **101**, 489 (1922).

Oxidations with permanganate under weakly acid, neutral, or alkaline conditions may take place in accordance with the equation:

$$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O$$

Here the hydrogen-ion concentration has less effect upon the oxidation potential than in more strongly acid solution. The direct titration of a neutral or alkaline solution presents a difficulty with end-point recognition, in that the precipitate of manganese dioxide must be allowed to settle before the color of the liquid can be judged. Nevertheless, such a procedure may under suitable conditions give good results, as in the determination of manganese and chromium. In some cases the oxidation requires a long time; the reagent is then added in excess and titrated back later. Reinitzer and Hoffmann[2] have investigated the composition of manganese dioxide precipitated under various experimental conditions.

Titrations with Alkaline Permanganate: Holluta[1] has shown that the reduction of permanganate by formate in not too weakly alkaline solution takes place in two distinct steps. Manganate is formed in the first step and is further reduced to manganese dioxide in the second. Of these two reactions the former has much the greater velocity, but the velocity of the latter is increased with an increase in hydroxyl-ion concentration. Oxidation potentials for the systems are given by Andrews and Brown[3] as follows:

$$MnO_4^- + e \rightleftharpoons MnO_4^{2-} \qquad (1)$$

$$E_1 = E_{0_1} - 0.0591 \log \frac{[MnO_4^{2-}]}{[MnO_4^-]}$$

$$E_{0_1} = 0.564$$

$$MnO_4^{2-} + 2H_2O + 2e \rightleftharpoons MnO_2(s) + 4OH^- \qquad (2)$$

$$E_2 = E_{0_2} - \frac{0.0591}{2} \log \frac{[OH^-]^4}{[MnO_4^{2-}]}$$

$$E_{0_2} = 0.60$$

$$MnO_4^- + 2H_2O + 3e \rightleftharpoons MnO_2(s) + 4OH^- \qquad \text{(sum of 1 and 2)} \quad (3)$$

$$E_3 = E_{0_3} - \frac{0.0591}{3} \log \frac{[OH^-]^4}{[MnO_4^-]}$$

$$E_{0_3} = 0.588$$

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[2] B. Reinitzer and F. Hoffmann, *Z. anal. Chem.*, **77**, 407 (1929). See also H. Stamm, *Die Reduktion von Permanganat zu Manganat als Grundlage eines neuen Titrationsverfahrens*, Akademische Verlagsgesellschaft, Halle, 1937.

[3] L. V. Andrews and D. J. Brown, *J. Am. Chem. Soc.*, **57**, 254 (1935).

The equilibrium constant for the reaction:

$$3MnO_4^{2-} + 2H_2O \rightleftharpoons 2MnO_4^- + MnO_2 + 4OH^-$$

is stated by Schlesinger and Siems[4] to have the value:

$$K = \frac{[MnO_4^-]^2[OH^-]^4}{[MnO_4^{-2}]^3} = 16 \pm 7$$

On the basis of practical and theoretical considerations, Stamm[2,5] introduced a new technique for permanganate titrations in alkaline solution. It depends upon repressing the manganate-ion concentration through addition of barium nitrate or chloride, so that the rapid reduction of permanganate to manganate is favored and the slower second step, manganate to manganese dioxide, scarcely proceeds at all. The solubility of barium manganate in water is very small, the solubility product being about 2.5×10^{-10} at 25°C.[4] The precipitate is finely granular, in contrast with the flocculent hydrous dioxide, and it settles out well. Its blue-green hue does not interfere with the perception of permanganate color at the end-point. It is more expedient, however, to titrate with the reducing agent in the burette and the permanganate in the beaker, since one may then titrate from red to colorless.

Since under these conditions the equivalent weight of permanganate is equal to the molecular weight, titrations are made with $0.1M$ solution rather than with the $0.02M$ solution ordinarily specified. The solution is prepared as described on p. 37, but with about 16 g. of potassium permanganate per liter. This higher concentration also increases the reaction rate. To determine substances which are oxidized slowly one may increase the quantity of alkali added, or warm the mixture gently for a brief period, in order to hasten the reaction. An excess of permanganate may be added and titrated back with a suitable reductant. In most cases the reaction velocity becomes quite low near the end of a titration. Stamm therefore suggests adding several drops of a dilute solution of some oxygen-accepting heavy metal such as copper, cobalt, nickel, or silver. The amount required is so small that the titration error involved is negligible.

Alkali hydroxide to be used in the titration must be very pure, especially with respect to reducing substances. Stamm recommends a grade prepared from sodium and sold in pellet form. As a titration vessel he employs a decantation flask of 300 ml. capacity, in one arm of which the precipitate is allowed to settle so that clear solution can be decanted into the other arm for observation.

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[4] H. I. Schlesinger and H. B. Siems, *J. Am. Chem. Soc.*, 46, 1965 (1924).

[5] H. Stamm, *Angew. Chem.*, 47, 791 (1934); cf. F. R. Duke, *J. Am. Chem. Soc.*, 70, 3975 (1948).

If the substance being analyzed contains sulfate, barium sulfate precipitates during the titration and occludes permanganate. Sulfate should therefore be removed beforehand, particularly if the reductant is to be run into the permanganate from a burette.

Stamm has outlined suitable conditions for the titration of formate, hypophosphite, phosphite, iodide and iodate (to periodate), cyanide, thiocyanate, methanol, formaldehyde, acetone, fumaric acid, and erythritol. He also suggests applications to the determination of metals, such as chromium, which have more than one valency state.

Many oxidation reactions are not reversible, this holding especially in the case of those organic substances which under suitable conditions are converted to carbon dioxide and water. The mechanisms are complicated and for the most part are not understood, so the optimum conditions have to be worked out empirically. Since even the reaction of oxalate with permanganate involves a rather elaborate system of kinetics (p. 48), the difficulties of interpreting more complex processes are not surprising.

The studies of Drummond and Waters[6] on the mode of action of alkaline permanganate on organic compounds are noteworthy. Evidence is given that the reduction of permanganate to manganate does not involve a free radical but a one-electron transfer: $MnO_4^- + e \rightleftharpoons MnO_4^{2-}$.

The above authors found that all classes of organic compounds except ethers, saturated carboxylic acids, including oxalic and pyruvic acids, and tertiary monohydric alcohols are oxidized considerably. The excess of permanganate is determined by making use of the reaction

$$2MnO_4^- + CN^- + H_2O \longrightarrow 2MnO_4^{2-} + CNO^- + 2H^+$$

An excess of cyanide is added, the mixture filtered, and the cyanide determined by argentometric titration (Liebig-Dénigès).

Recently Issa and Awad[7] have made the interesting observation that, when divalent tin is oxidized with permanganate in weakly alkaline solutions, trimanganese tetroxide, Mn_3O_4, is formed, the reaction being formulated

$$6MnO_4^- + 13SnO_2^{2-} + 3H_2O \longrightarrow 2Mn_3O_4 + 13SnO_3^{2-} + 6OH^-$$

2. Preparation, Stability, and Use of Permanganate Solutions. Potassium permanganate of relatively high purity is available commercially but should not be relied upon as a primary standard.

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[6] A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, **1953**, 435.

[7] I. M. Issa and S. A. Awad, *J. Indian Chem. Soc.*, 32, 23 (1955).

Products containing traces of chloride, sulfate, and nitrate, and possessing effective strengths varying from 99.0 to 99.6 per cent, have been encountered.[8] Qualitative testing for purity is rather difficult. By recrystallizing from water one may obtain a product assaying from 99.6 to 99.8 per cent, but if this is weighed out exactly for preparation of a standard solution the latter is likely to be somewhat weaker than expected. Small amounts of reducing substances are generally present in the water used, even in distilled water of otherwise good quality. Therefore it is best to prepare a solution from slightly more than the calculated quantity of permanganate, and to standardize it after boiling and cooling.

Preparation: For $0.1N$ solution, dissolve 3.2 g. of potassium permanganate in 1 liter of distilled water and heat to boiling, or keep for an hour on the steam bath. Filter through pure asbestos or a sintered-glass crucible of fine porosity (never through filter paper). The filtered solution should be kept in the dark, preferably in a clear glass bottle painted black on the outside, and should be protected from evaporation and exposure to reducing vapors or dust. A glass-stoppered bottle, previously rinsed with potassium bichromate–sulfuric acid cleaning mixture to remove organic matter and finally with distilled water, should be used. If in time the solution deposits traces of manganese dioxide, it should be filtered again and restandardized.

Zavgorodnii[9] recommends boiling the solution for 1 hour. He then adds 10–15 g. of kaolin, previously dried at 200°C., and filters through sintered glass. He claims that this treatment provides a very stable solution.

The best way to prepare $0.01N$ permanganate is to dilute $0.1N$ solution with water that has been freed from reducing substances by distillation over permanganate.

Stability: The oxidation potential of a permanganate solution is higher than that of an oxygen electrode, particularly in the presence of acid. It follows that acidification renders a permanganate solution less stable. This has been amply substantiated by the experiments of Vorländer and coworkers[10] and of Kolthoff.[11] A solution that is $0.04N$ in sulfuric acid decomposes nearly twenty times as rapidly as a neutral solution. On the other hand, decomposition also takes place rapidly if sodium carbonate or hydroxide is added.

Manganous salts and manganese dioxide promote the decomposition of permanganate. According to Morse, Hopkins, and Walker,[12] oxygen is liberated:

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[8] I. M. Kolthoff, unpublished investigations; cf. G. Bruhns, *Chem. Ztg.*, **47**, 613 (1923).

[9] S. F. Zavgorodnii, *Zavodskaya Lab.*, **15**, 363 (1949).

[10] D. Vörlander, G. Blau, and T. Wallis, *Ann.*, **345**, 261 (1906).

[11] I. M. Kolthoff, *Pharm. Weekblad*, **61**, 337 (1924).

$$2HMnO_4 + xMnO_2 \qquad \cdot (x + 2)MnO_2 + 3O + H_2O$$

More manganese dioxide is formed in the process; hence the action is autocatalytic. The effect of manganous ions is similar since these ions react with permanganate to yield the hydrated dioxide.

The studies of various workers[11,13] indicate that a neutral $0.1N$ permanganate solution, carefully freed from impurities and kept in the dark, should not decrease in titer by more than 0.2 per cent in 6 months. A $0.01N$ solution, prepared by diluting $0.1N$ permanganate with pure water, is likely to show a decrease of 0.2 per cent a month under the same conditions. A similar solution exposed to diffused daylight may lose nearly 20 per cent of its oxidizing capacity in a month.

General Notes on the Use of Permanganate Solution: Because of the dark color of $0.1N$ permanganate solution, it is customary to make burette readings at the upper surface of the liquid. Use of a white reading card is helpful. With more dilute solutions readings are made in the usual way, tangent to the meniscus. Permanganate should not be allowed to remain in the burette for more than a short time, since photochemical decomposition takes place and manganese dioxide is deposited upon the walls. A burette contaminated in this way is most readily cleaned with strong hydrochloric acid.

If, as is commonly the case, a solution is to be acidified before titration with permanganate, the acid used must be free from reducing substances. A simple blank test is not adequate, since some impurities (such as phosphorous acid in phosphoric) react very slowly with permanganate alone but undergo induced oxidation during the titration of another compound. Therefore it is better to treat an acidified blank with 10 ml. of permanganate and to titrate back after it has stood for several hours in the dark.

When the direct oxidation of a compound with permanganate proceeds slowly, it is customary to add an excess of oxidant and later determine this in acid solution, either by introducing an excess of oxalic acid, ferrous iron, or hydrogen peroxide, which may be titrated with permanganate to a pink color, or by adding potassium iodide and titrating the liberated iodine with thiosulfate.

Sometimes it is necessary to determine a substance in the form of a precipitate, such as calcium oxalate, which must first be collected on a filter. Some workers have advised that filter paper be kept from contact with the solution during titration, while others have ignored the possibility of interference. Curtis and Finkelstein[14] demonstrated that there is a definite overconsumption of permanganate if filter paper is present during the titration of oxalate. They prefer to filter on asbestos fiber, which does not interfere. Filtration on a sintered-glass or porous porcelain crucible is also to be recommended for such cases.

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[12] H. N. Morse, A. J. Hopkins, and M. S. Walker, *Am. Chem. J.*, **18**, 401 (1896).

[13] G. Lunge, *Z. angew. Chem.*, **18**, 1520 (1905); F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Vol. II, Dueticke, Vienna, 1907; G. Bruhns, *Z. anorg. Chem.*, **49**, 277 (1906); B. Grützner, *Arch. Pharm.*, **230**, 321 (1892); T. Kato, *J. Chem. Soc. Japan*, **48**, 17 (1927).

In any titration involving an excess of permanganate, one must consider the probability of autodecomposition with liberation of oxygen. The extent to which this may occur is dependent upon the concentrations of permanganate, manganese, and hydrogen ions, the time and temperature,[15] and the amount of manganese dioxide present. The effect of acidity has been shown in tests by Noll,[16] who boiled 100 ml. of diluted sulfuric acid and 12 ml. of $0.1N$ permanganate for 10 minutes, in the presence of some pumice chips to prevent bumping. He obtained the following results:

Sulfuric acid normality:	0.4	0.8	1.2	1.6	3.2	4.8	6.4	8.0
Permanganate loss, %:	0.6	0.8	0.9	1.0	1.8	3.5	6.2	10.1

Manganese dioxide is a strong catalyst for permanganate decomposition as has already been mentioned. A pure $0.05N$ permanganate solution, $0.4N$ in sulfuric acid, lost 0.6 per cent of its oxidizing strength upon being kept for an hour at 100°C. After the experiment was repeated with the addition of 1 mg. of manganous ion (which with permanganate forms manganese dioxide) the final titer had decreased by 46 per cent. At other temperatures the results are about what would be expected from those given above.

Decomposition on heating is also marked in alkaline solution,[17] but neutral solutions are much more stable even in the presence of manganous ion. This may be explained by the hypothesis that manganese dioxide formed in neutral solution exerts little or no action upon permanganate, whereas in acid solution it behaves like hydrogen peroxide:

$$MnO_2 + H_2SO_4 \longrightarrow H_2O_2 + MnSO_4$$

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \longrightarrow 2MnSO_4 + 5O_2 + K_2SO_4 + 8H_2O$$

More dilute permanganate solutions ($0.01N$ or less) behave in the same way as $0.1N$ solutions, although the self-decomposition is relatively smaller.

From the foregoing it follows that one cannot in general expect good results from heating a substance with excess permanganate and then titrating the excess. The longer the solution is warmed, the greater the error becomes. In the literature it is usually specified that a blank be run under the same conditions, but the quantity of manganous ion formed in a blank is smaller and therefore the autodecomposition is less.

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[14] R. W. Curtis and J. Finkelstein, *Ind. Eng. Chem., Anal. Ed.*, **5**, 318 (1933).

[15] Cf. F. Schulze, referred to by Schacht, *Arch. Pharm.*, **185**, 12 (1868); F. A. Gooch and E. W. Danner, *Am. J. Sci.*, **144**, 301 (1892); D. Vorländer, G. Blau, and T. Wallis, *Ann.*, **345**, 261 (1906); A. Skrabal, *Monatsh.*, **27**, 535 (1906); *Z. anorg. Chem.*, **68**, 48 (1910); A. C. Sarkar and J. M. Dutta, *ibid.*, **67**, 225 (1910); J. O. Halverson and O. Bergeim, *Ind. Eng. Chem.*, **10**, 119 (1918); *Am. J. Pharm.*, **90**, 358 (1918).

[16] A. Noll, *Z. angew. Chem.*, **24**, 1509 (1911).

[17] For data on the velocity of manganate formation see R. H. Ferguson, W. Lerch, and J. E. Day, *J. Am. Chem. Soc.*, **53**, 126 (1931).

By heating quite dilute (0.002 to 0.01*N*) permanganate solution in 5 per cent sulfuric acid for 15 minutes on a water bath, Ernst and Horvath[18] found very little spontaneous formation of manganous ions. They then treated similar solutions with varying amounts of 0.01*N* oxalic acid and observed a strict proportionality between the total permanganate consumption and the quantity reduced spontaneously. For micro determinations one can empirically construct a correction curve to compensate for the error. Whether the same can be done for macro work remains to be seen. It would be desirable to know also whether self-reduction can be inhibited by anions such as those of hydrofluoric and metaphosphoric acids, which form stable complexes with manganese.

Since the heating of permanganate cannot be recommended, Kolthoff carried out a series of tests at lower temperature. In each case the solution was 0.05*N* in permanganate, had a total volume of 50 ml., and was allowed to stand in a closed vessel for the period indicated (probably at about 15°C.).

TABLE I

Decomposition of Unheated 0.05*N* Permanganate Solutions

Concentration of acid or alkali, *N*		Manganese addition (mg. Mn^{2+})	Time of standing (hr.)	Decrease in titer (%)
	0	0	24	0.0
	0	0	48	0.0
H_2SO_4	0.4	0	24	0.7
	0.7	0	24	1.2
	0.4	10	24	0.8
	0.4	20	24	0.85
NaOH	0.6	0	24	0.4
	0.6	0	48	0.4
	1.0	0	24	0.8
	1.0	0	48	0.8

Similar experiments were made with 0.01*N* permanganate; here also the decomposition was shown to be slight in not too strongly acid solution, even with manganous ions present. In view of these facts, the following recommendation is made:

To determine a substance which is slowly oxidized by permanganate, it should be treated with an excess of the oxidant at room temperature. The solution is brought to the optimum acidity or alkalinity and is set aside in a stoppered flask until the oxidation is complete. The excess of permanganate is then determined. A blank test should be run under the same conditions.

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[18] E. Ernst and G. Horvath, *Biochem. Z.*, 224, 135 (1930).

Practical applications of this procedure to the determination of various reducing agents are given in the next chapter.

3. Standardization of Permanganate Solutions. The most popular substance for standardizing permanganate is sodium oxalate. For reasons that will appear later, however, arsenic trioxide and potassium iodide deserve preference.

Arsenic Trioxide (As_2O_3, equivalent weight 49.45): Impure arsenic trioxide is ordinarily purified by recrystallization first from hot 20 per cent hydrochloric acid and then repeatedly from water, until the mother liquor is no longer acid to methyl yellow. The crystalline powder so obtained is dried to constant weight over sulfuric acid in a desiccator.

Chapin[19] noted that a product purified by crystallization or sublimation[20] may still contain antimony trioxide. Foulk and Horton[21] therefore proposed the following treatment. Dissolve 150 g. of the crude material in 350 ml. of concentrated hydrochloric acid and distill in a stream of hydrogen chloride gas from a suitable generator. Cool the vapors in an ordinary water condenser provided with an adapter, the latter reaching nearly to the bottom of an ice-cooled Erlenmeyer flask which serves as the receiver. More arsenic trioxide may be added to the distilling flask from time to time. The distillate separates into two layers: arsenic trichloride and hydrochloric acid. Since antimony chloride is more soluble in the concentrated acid, the arsenic chloride may be purified by several extractions. The lower layer is drawn off and shaken for 1 minute with two thirds its volume of fresh hydrochloric acid. About 10 per cent of the arsenic is lost through solubility during each extraction. When the last acid wash shows no test for antimony (see purity tests), the lower layer is allowed to run slowly and with vigorous stirring into a large beaker of boiling water. Arsenic trioxide separates as a fine white powder upon cooling; it is filtered out, washed free of acid, recrystallized from water, and dried.

Standard arsenic trioxide of 99.99 per cent active strength against iodine may be obtained from the National Bureau of Standards (Sample 83a). This is stated to contain 0.002 per cent nonvolatile matter and less than 0.002 per cent antimony.

Tests for Purity—Ignition Residue: Five grams of the oxide is ignited in a tared porcelain crucible, the operation being carried out in an efficient hood because the fumes are poisonous. Much of the material may be recovered as a sublimate. The residue should not exceed 0.5 mg. (0.01 per cent).

Since the ignition is unpleasant, Kolthoff[22] proposed to test for electrolytes through conductivity measurements. The specific conductance of a saturated solution of pure arsenic trioxide at 18°C. is 1×10^{-5} ohm^{-1}. In order to exclude more than 0.01 per cent of foreign electrolyte, a saturated solution should have a conductivity not greater than 2×10^{-5} at 18°. Silicic acid cannot be detected by this method.

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[19] R. M. Chapin, *Ind. Eng. Chem.*, **10**, 522 (1918).

[20] According to G. P. Baxter and W. E. Shaefer, *J. Am. Chem. Soc.*, **55**, 1957 (1933), arsenic trioxide cannot be obtained pure by sublimation. Some pentoxide is formed upon heating in air, whereas a trace of elemental arsenic seems to be produced by subliming *in vacuo*.

[21] C. W Foulk and P. G. Horton, *J. Am. Chem. Soc.*, **51**, 2416 (1929).

[22] I. M. Kolthoff, *Z. anal. Chem.*, **60**, 394 (1921).

Arsenic Pentoxide: A solution of arsenic acid reacts strongly acid; the first dissociation constant is 5×10^{-3}, or about 10^7 times that of arsenious acid. Upon boiling 1 g. of arsenic trioxide with 20 ml. of water for half a minute, the filtrate after cooling should react neutral to methyl yellow; sensitivity, 0.02 per cent As_2O_5. Kolthoff found 0.06 per cent As_2O_5 in a Kahlbaum product containing 0.064 per cent ash.

Sulfides: No color change should take place upon adding 0.1 ml. of 0.5*N* lead acetate to a solution of 5 g. arsenic trioxide in 20 ml. of 25 per cent sodium hydroxide.

Antimony: Dissolve 10 g. of arsenic trioxide in 25 ml. of concentrated hydrochloric acid in a distillation flask. (To test a product being prepared by the Foulk and Horton method, use the acid layer directly.) Distill just long enough to remove dissolved oily arsenic trichloride, so that the distillate comes over clear. Transfer the residue to a beaker and, while it is still hot, pass in hydrogen sulfide to precipitate the remaining arsenic. Filter on a glass crucible, dilute the filtrate with three times its volume of water, and saturate again with hydrogen sulfide. An orange precipitate indicates antimony. The sensitivity (on a 10 g. sample) is 0.01 per cent; if the solution is allowed to stand for a day or so the test becomes still more sensitive.

Moisture: Although crystalline arsenic trioxide is not hygroscopic, the so-called amorphous material can apparently take up about 1 per cent water. A 10 g. portion of acceptable material should not lose more than 1 mg. on drying to constant weight over sulfuric acid.

Chloride: Ten milliliters of a 1 per cent solution of the trioxide, acidified with nitric acid and treated with silver nitrate, should show no turbidity or opalescence; sensitivity, 0.01 per cent.

Preparation and Stability of Arsenious Solutions: 0.1*N* solutions of arsenic trioxide are quite stable if neutral or weakly acid, but unstable if strongly acid or alkaline.[23] Table II shows the decreases in

TABLE II

Reagent added (per 100 ml.)	Decrease in titer (%)
None (pH 7.0)	0.0
20 ml. 2*N* $(NH_4)_2CO_3$	0.0
20 ml. 2*N* Na_2CO_3	0.0
4 ml. 4*N* NaOH	16.5
20 ml. 4*N* HCl	0.5

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[23] I. M. Kolthoff, *Z. anal. Chem.*, **60**, 393 (1921); F. Reinthaler, *Chem. Ztg.*, **36**, 713 (1912).

titer noted after keeping $0.1N$ solutions for 2 months (at 15–18°C.).

It is apparent that a nearly neutral solution is to be preferred. Substances which may catalyze air-oxidation should be excluded; according to Reinders and Vles[24] copper is an active catalyst, particularly in alkaline medium. Finely divided or porous materials such as charcoal may also accelerate oxidation to arsenate.

Preparation of 0.1N Solution: Weigh out 4.945 g. of pure dry arsenic trioxide and dissolve in 60 ml. of $1N$ sodium hydroxide. Neutralize with 59–60 ml. of $1N$ hydrochloric or sulfuric acid and dilute to 1000 ml. The solution should react neutral to litmus paper.

Standardization of Permanganate: The reduction of permanganate by arsenic trioxide in sulfuric acid solution takes place quite smoothly at first, but soon there are formed yellow, green, or brown manganic compounds which react only gradually. In hydrochloric acid at room temperature the phenomena are similar; at higher temperature the reduction proceeds more rapidly, and a direct titration is possible if the solution is boiled near the end. It is much better to add a catalyst for the reaction. C. Lang[25] found traces of iodide and bromide to be effective. According to R. Lang[26] iodate can be used as well as iodide. The precision and accuracy of Lang's method have been studied by Kolthoff, Laitinen, and Lingane[27] and by Bright;[28] agreement to within 1 part in 3000 was found in Bright's comparison of arsenic trioxide and sodium oxalate as standard substances.

The titration may be carried out potentiometrically or visually. Permanganate serves as its own indicator, but a correction is necessary for the excess needed to reveal the end-point. The correction, which should not amount to much more than 0.03 ml. of $0.1N$ solution, is determined by titrating a blank with as much alkali, acid, catalyst, and water as would ordinarily be present. It is advantageous to use *o*-phenanthroline-ferrous sulfate (ferroin) as indicator, since the correction is then smaller.

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[24] W. Reinders and S. I. Vles, *Rec. trav. chim.*, 44, 29 (1925).

[25] C. Lang, *Chem. Ztg.* (*Repertorium Sect.*), 29, 48 (1905).

[26] R. Lang, *Z. anorg. u. allgem. Chem.*, 152, 203 (1926); O. Cantoni, *Ann. chim. appl.*, 16, 153 (1926); O. Pročke and J. Švéda, *Chem. Zentr.*, 1926 (I), 1859; *Chem. Abstr.*, 21, 3577 (1927).

[27] I. M. Kolthoff, H. A. Laitinen, and J. J. Lingane, *J. Am. Chem. Soc.*, 59, 429 (1937).

[28] H. A. Bright, *Ind. Eng. Chem., Anal. Ed.*, 9, 577 (1937).

Metzler, Myers, and Swift[29] find that with only a small quantity of iodide or iodate as catalyst, and with ferroin as indicator, the titration becomes very slow at the end-point. Therefore they recommend using more catalyst and introducing it in the same form that it should assume at the end. Iodine monochloride is the proper form if the solution titrated is about $0.6N$ in hydrochloric acid.

Procedure with Iodate as Catalyst: Pipette 50 ml. of $0.1N$ arsenic trioxide solution into a 400 ml. beaker and add 15 ml. of $6N$ hydrochloric acid, or weigh out accurately about 0.25 g. of dry arsenic trioxide, dissolve it in 10 ml. of $4N$ sodium hydroxide free from reducing substances, and add 20 ml. of $6N$ hydrochloric acid. In either case, introduce enough water to make the volume about 120 ml. and add 1 drop of $0.0025M$ potassium iodate as well as 1 g. of sodium chloride. Titrate with permanganate until the color fades rather slowly after each addition, then add 2 drops of $0.025M$ ferroin indicator (p. 127). Complete the titration dropwise, waiting for the pink color to return after each drop before adding more reagent. At the end-point the indicator changes permanently to a very faint blue.

Procedure with Iodine Monochloride as Catalyst: Pipette 50 ml. of $0.1N$ arsenic trioxide solution into 50 ml. of water containing 6 ml. of $11N$ hydrochloric acid and 1 g. of sodium chloride. Add 1 ml of $0.0025M$ iodine monochloride solution (Note 1) and titrate rapidly with permanganate until a lag in the rate of decolorization is noticed. Continue the titration dropwise and with stirring until the pink color spreads almost throughout the solution. Introduce 0.04 ml. of $0.025M$ ferroin and complete the titration to a point at which the pink ferroin color can no longer be detected. Titrate a blank solution in the same way and subtract from the result; only about 0.01 or 0.02 ml. of $0.1N$ permanganate should be required.

Notes: (1) Iodine monochloride solution ($0.0025M$ or $0.005N$) is prepared by titrating a potassium iodide solution in $4N$ hydrochloric acid with potassium iodate until upon shaking with a little carbon tetrachloride no iodine color remains in the organic layer. A portion of the aqueous layer is then standardized with sodium thiosulfate in the presence of water and more potassium iodide, and another portion is diluted accordingly with $4N$ hydrochloric acid.

(2) Metzler, Myers, and Swift,[29] working with weight burettes and completing the titration with $0.01N$ permanganate from a 10 ml. burette, found the average deviation of their original procedure to be less than 0.01 per cent and the maximum deviation 0.03 per cent.

Gleu[30] demonstrated that traces of osmium tetroxide (osmic acid) catalyze the reaction of arsenious acid with permanganate in sulfuric acid solution. In his procedure, the weighed quantity of arsenic trioxide is dissolved in 10 ml. of 1 or $2N$ alkali and treated with 50 ml. of $1N$ sulfuric acid. To the solution there are added 3 drops of $0.01M$ osmium tetroxide in $0.1N$ sulfuric acid, and the mixture is titrated with permanganate to a faint permanent pink. The end-point is sharp, but a blank correction should be determined and subtracted.

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[29] D. E. Metzler, R. J. Myers, and E. H. Swift, *Ind. Eng. Chem., Anal. Ed.*, **16**, 625 (1944).

[30] K. Gleu, *Z. anal. Chem.*, **95**, 305 (1933).

Potassium Iodide (KI; molecular weight, 166.02; rational, 165.98): For most practical purposes potassium iodide of analytical reagent grade is sufficiently pure to be used for standardizing permanganate solutions. Kolthoff and Laitinen[31] tested one C.P. product and found it to be 99.94 per cent pure after drying at 250 °C. For very accurate work, however, one should either test the purity or use material prepared by the following method.

Preparation: Kolthoff, Laitinen, and Lingane[32] prepared potassium iodide from potassium bicarbonate and pure hydriodic acid. The latter is made directly from hydrogen and iodine in the all-glass apparatus shown in Fig. 1.

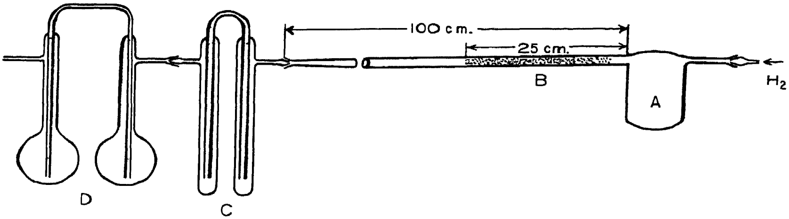

FIG. 1. Apparatus for preparation of pure hydriodic acid.[32]

The joints of this apparatus are lubricated with a little phosphoric acid, except for the one between C and D, which is sealed with a drop of water. B is a porous plug of platinized asbestos. Iodine, previously resublimed from potassium iodide, is placed in bulb A and nitrogen is introduced through the short arm until the apparatus is flushed out well. Then hydrogen is passed through in place of nitrogen, the right end of the plug is heated to about 400 °C. with a burner, and bulb A is immersed in an electrically heated glycerol bath at 150–180°. Iodine vaporizes and reacts, the resulting hydrogen iodide being cooled by an ice-salt bath at trap C to remove free iodine and collected in conductivity water in the absorption bulbs at D.

The rate of hydrogen flow during a run is adjusted so that about 2–3 bubbles per second escape from the absorption bulbs. The rate of reaction can be controlled by regulating the temperature of A and the flow of hydrogen. In a typical run 180 g. of iodine was reduced in 6 hours, with a hydriodic acid yield of better than 95 per cent.

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[31] I. M. Kolthoff and H. A. Laitinen, *J. Am. Chem. Soc.*, **61**, 1690 (1939).

[32] I. M. Kolthoff, H. A. Laitinen, and J. J. Lingane, *J. Am. Chem. Soc.*, **59**, 429 (1937).

The acid solution is treated with a slight deficiency of potassium bicarbonate, previously recrystallized several times from water at 70°C. in an atmosphere of carbon dioxide. The resulting solution of potassium iodide and excess acid is evaporated to crystallization in a stream of hydrogen. With hydrogen still passing through, the mixture is cooled, then the crystals are collected on a glass filter, sucked dry, and eventually stored in a desiccator over fused potassium hydroxide. For removal of the last traces of water the salt is fused in a platinum boat, in a current of pure, dry hydrogen. The product is neutral, pure, and only slightly hygroscopic.[33] In case the fusion is omitted and the salt is dried at 200–225° instead, it will contain only about 0.025 per cent moisture; fusion is therefore unnecessary for practical work.

Tests for Purity—Bromide and Chloride: Dissolve 1 g. of potassium iodide in 10 ml. water and add 5 ml. of 4*N* sulfuric acid; then, while shaking thoroughly, pour in 1 g. of halide-free sodium nitrite dissolved in 10 ml. water. Filter off the liberated iodine, boil the filtrate for 5 minutes, cool, and dilute to 20 ml. Upon testing with silver nitrate, no more turbidity should result than appears in a blank solution to which 0.1 mg. of chloride ion has been added. Sensitivity, 0.01 per cent Cl.

Alkalinity: A solution of 1 g. potassium iodide in 10 ml. of distilled water should react not quite completely alkaline to methyl red (pH between 5.0 and 6.2).

Standardization of Permanganate against Potassium Iodide: Because iodine has such an intense color, the titration of iodide with permanganate must be carried out either potentiometrically[34] or in the presence of some substance capable of combining with iodine. Kolthoff, Laitinen, and Lingane[32] found a precision of 0.005 per cent in the potentiometric method. Less precise though still useful results are obtained with the methods of Lang, Andrews, and Berg outlined below.

Iodine Cyanide Procedure of Lang:[35] When iodide is oxidized in the presence of hydrocyanic acid, colorless iodine cyanide is formed:

$$I^- + HCN \rightleftharpoons ICN + H^+ + 2e$$

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[33] I. M. Kolthoff and J. J. Lingane, *J. Am. Chem. Soc.*, 58, 1524 (1936).

[34] W. S. Hendrixson, *J. Am. Chem. Soc.*, 43, 14, 858 (1921); I. M. Kolthoff, *Rec. trav. chim.*, 40, 532 (1921).

[35] R. Lang, *Z. anorg. u. allgem. Chem.*, 122, 332 (1922); cf. N. McCulloch, *Chem. News*, 57, 135 (1888).

The equivalent weight of potassium iodide as a reductant in this sense is half the molecular weight.

An accurately weighed portion of the salt is dissolved in 25 ml. of water and is treated with 50 ml. of $4N$ sulfuric acid and 10–20 ml. of $0.5N$ potassium cyanide. The solution is titrated nearly to the equivalence point with permanganate, then 20 ml. of 0.2 per cent starch solution is added and the titration is continued until the mixture becomes colorless. This end-point generally appears too early, by about 0.07 per cent. Next 2 drops of $0.025N$ ferroin indicator (p. 127) are introduced and the permanganate is added in small increments, to a change from red to practically colorless. Ferroin must not be added before the starch-iodine end-point, because it would react with iodine.

In titrating 1–1.3 g. portions of potassium iodide with $0.5N$ permanganate, results were found to be reproducible within ±0.03 per cent and the average normality was 0.04 per cent higher than that obtained potentiometrically.

Iodine Chloride Procedure of Andrews:[36] In principle this method is similar to Lang's:

$$I^- + HCl \rightleftharpoons ICl + H^+ + 2e$$

The end-point is determined with the aid of carbon tetrachloride to concentrate the last traces of iodine.

About 25 ml. of water and 1 ml. of concentrated hydrochloric acid are placed in an iodine flask and pure potassium bicarbonate is added in small portions until a slight excess is present and most of the air in the flask has been replaced by carbon dioxide. The weighed amount of potassium iodide is then introduced and the solution is diluted to 100–125 ml. (In case the iodide has been fused in a platinum boat, the boat is placed directly in the flask and is removed, after solution of the salt, with a hooked glass rod; boat and rod should be rinsed well with water.) Enough concentrated ($12N$) hydrochloric acid is added to make the final acidity from 3.7 to $5.5N$ at the end-point. The solution is cooled in an ice bath and treated with 5 ml. of carbon tetrachloride, after which the titration with permanganate is begun. When the iodine color that is first formed finally disappears from the carbon tetrachloride layer after thorough shaking, the end-point has been reached. The permanganate normality so found is likely to be 0.04 per cent low.

Acetone Method of Berg:[37] The following procedure was found to give results accurate to within 0.1 per cent in the standardization of $0.1N$ permanganate. However, in the standardization of a $0.01N$ solution the normality obtained was 0.8 to 1.0 per cent low.[38]

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[36] L. W. Andrews, *J. Am. Chem. Soc.*, **25**, 756 (1903); *Z. anorg. Chem.*, **36**, 76 (1903).

[37] R. Berg, *Z. anal. Chem.*, **69**, 369 (1926); D. Lewis, *J. Am. Chem. Soc.*, **59**, 1401 (1937).

[38] I. M. Kolthoff and H. A. Laitinen, *J. Am. Chem. Soc.*, **61**, 1690 (1939).

Approximately 0.35 g. of potassium iodide is weighed exactly, dissolved in 75 ml. of water, and treated with 5 ml. of $18N$ sulfuric acid. Three drops of $0.025N$ ferroin indicator and 20–25 ml. of C.P. acetone are added and the well-mixed solution is titrated with permanganate to a change from red to practically colorless which persists for 30 seconds.

Note: The procedure described can also be used in standardizing ceric sulfate (p. 135).

Potassium Iodate (KIO_3; molecular weight, 214.02; rational, 213.96): This salt can easily be obtained in pure form (Vol. II, p. 88). Sulfurous acid reduces it to iodide, which can be titrated by one of the methods previously described.

Procedure:[39] Place a weighed portion of potassium iodate in a glass-stoppered Erlenmeyer flask and dissolve in 50 ml. of water. Treat with 10 ml. of $4N$ sulfuric acid and then add 10 per cent sodium sulfite solution until the iodine that is liberated at first dissolves again and finally disappears completely. If the theoretical quantity of sulfite is added, the solution becomes colorless; excess sulfurous acid forms a yellow complex with hydriodic acid. In order to avoid loss of iodine by vaporization, the reduction should be done quickly and the flask should be stoppered and shaken after each addition of sulfite. Better yet, the required amount of sulfite can be added all at once. Any excess sulfurous acid is expelled by boiling the solution until a starch-iodate paper test of the vapor is negative. Cool the solution, add reagents appropriate to the method chosen, and titrate.

Sodium Oxalate and Oxalic Acid ($Na_2C_2O_4$, equivalent weight 67.01, rational 66.99; $H_2C_2O_4 \cdot 2H_2O$, equivalent weight 63.03, rational 63.00): The preparation methods and purity tests for these substances are given in Volume II, pp. 74 and 95. Sodium oxalate of 99.95 per cent purity by titration is available from the National Bureau of Standards (Sample 40d).

When permanganate is added to a solution of oxalic acid, the color does not fade at once. As was pointed out in Vol. I, p. 173, the reaction is quite complicated. Skrabal[40] suggested that there are periods of incubation and induction during which di-, tri-, and tetravalent manganese ions are formed slowly, followed by a final period in which the oxides of intermediate valence react rapidly with oxalic acid. If a little manganous salt is added, permanganate is consumed almost immediately at higher temperature. Manganous ion therefore appears to act as a catalyst; Riesenfeld and Chang,[41] however, believe that the catalysis is actually brought about by higher oxides of manganese. Although the question of reaction mechanism cannot yet be regarded as completely clarified, the scheme suggested by Launer and Yost[42] seems to be in harmony with most of the experimental facts:

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[39] I. M. Kolthoff, *Z. anal. Chem.*, **64**, 260 (1924).

[40] A. Skrabal, *Z. anorg. Chem.*, **42**, 1 (1904); *Die induzierten Reaktionen*, Sammlung chemischer Vorträge, Stuttgart, 1908.

$$2MnO_4^- + 3Mn^{2+} + 16H^+ \longrightarrow 5Mn^{4+} + 8H_2O \quad \text{(rapid)} \qquad (a)$$

$$Mn^{4+} + Mn^{2+} \longrightarrow 2Mn^{3+} \quad \text{(rapid, reversible)} \qquad (b)$$

$$Mn^{4+} + C_2O_4^{2-} \longrightarrow Mn^{3+} + CO_2 + CO_2^- \quad \text{(measurable)} \qquad (c)$$

$$Mn^{4+} + CO_2^- \longrightarrow CO_2 + Mn^{3+} \quad \text{(rapid)} \qquad (d)$$

$$Mn^{3+} + 2C_2O_4^{2-} \longrightarrow Mn(C_2O_4)_2^- \quad \text{(rapid, reversible)} \qquad (e)$$

$$Mn^{3+} + C_2O_4^{2-} \longrightarrow Mn^{2+} + CO_2 + CO_2^- \quad \text{(measurable)} \qquad (f)$$

$$Mn^{3+} + CO_2^- \longrightarrow Mn^{2+} + CO_2 \quad \text{(rapid, but slower than } d) \qquad (g)$$

The reaction between permanganate and oxalate ion is extremely slow, whereas that between trivalent or tetravalent manganese ion and oxalate ion is measurable, according to the authors named above. They assume that some tetrapositive manganese ion is formed intermediately by the reaction between permanganate and oxalate, but that more is produced quickly by reaction (*a*) if a manganous salt is added. In case the concentration of manganous salt is small and that of oxalate is large, the latter is oxidized mainly by Mn^{4+}, with transient formation of CO_2^- (*c*). In the reverse case, however, Mn^{3+} is formed so that reactions (*e*), (*f*), and (*g*) predominate. Between these extremes, all the reactions take place.

Bradley and van Praagh[43] noted that at low acidity the formation of hydrous manganese dioxide hinders the oxidation of oxalic acid, because reaction with the precipitate can take place only at the surface. They emphasized also that oxalate itself retards the reaction by forming a complex with trivalent manganese ions; for the complex they suggested the formula $[Mn(C_2O_4)_3]^{3-}$ since the hydrated potassium salt of this ion has been isolated.[44] Barredo and Senent[45] in a photographic study found the reaction of permanganate with oxalate in acid solution to be first order throughout, a fact which they attribute to the formation and measurable decomposition of $[Mn(C_2O_4)_3]^{3-}$. Other ions which yield manganic complexes, such as fluoride, phosphate, and arsenate, also hinder the oxidation of oxalate. Increase in hydrogen-ion concentration, on the other hand, favors oxidation. According to Mapstone and Smith[46] ferric ions exert a catalytic effect on the oxidation of oxalic acid with permanganate and enable the titration to be made at room temperature, although the reaction is rather slow. In bright sunlight the reaction is three and a half times as fast as in diffuse daylight.

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[41] E. H. Riesenfeld and T. L. Chang, *Z. anorg. u. allgem. Chem.*, **230**, 239 (1937).

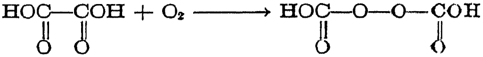
[42] H. F. Launer and D. M. Yost, *J. Am. Chem. Soc.*, **56**, 2571 (1934). See also H. F. Launer, *ibid.*, **54**, 2597 (1932); R. W. Fessenden and B. C. Redmon, *ibid.*, **57**, 2246 (1935); O. M. Lidwell and R. P. Bell, *J. Chem. Soc.*, **138**, 1303 (1935).

[43] J. Bradley and G. van Praagh, *J. Chem. Soc.*, **141**, 1624 (1938); cf. F. C. Tompkins, *Trans. Faraday Soc.*, **38**, 131 (1942).

[44] G. H. Cartledge and W. P. Ericks, *J. Am. Chem. Soc.*, **58**, 2061 (1936).

[45] J. M. Gonzalez Barredo and S. Senent, *Naturwiss.*, **31**, 550 (1943). See also M. J. Polissar, *J. Am. Chem. Soc.*, **58**, 1372 (1936).

If the solution contains oxygen, a peroxide-like substance may be formed during the oxidation of oxalic acid.[47,48] Deiss[49] assumed that the acid first forms an unstable peroxide:



$$\underset{\underset{\displaystyle O}{\|}}{HOC}-\underset{\underset{\displaystyle O}{\|}}{COH}+O_2\longrightarrow\underset{\underset{\displaystyle O}{\|}}{HOC}-O-O-\underset{\underset{\displaystyle O}{\|}}{COH}$$

The direct formation of peroxalic acid does not seem plausible. It is known that free organic radicals generally react quickly with oxygen to form hydroperoxide free radicals. Thus Launer[50] postulated that the hypothetical free radical ion CO_2^- (p. 49), which is assumed to be an unstable intermediate reaction product, reacts rapidly with oxygen:

$$CO_2^- + O_2 \longrightarrow O{-}O{-}CO_2^-$$
$$O{-}O{-}CO_2^- + Mn^{2+} + 2H^+ \longrightarrow Mn^{3+} + CO_2 + H_2O_2$$

Launer's interpretation does not appear to be in harmony with the fact that the formation of hydrogen peroxide through reaction with oxygen does not affect the analytical result. Kolthoff[51] offers the following explanation. A free radical ion $C_2O_4^-$, that is formed during the titration reacts with oxygen:

$$\begin{array}{rcl} C_2O_4^- + O_2 & \longrightarrow & O_2^- + 2CO_2 \\ O_2^- + H^+ & \longrightarrow & HO_2 \\ \underline{H^+ + HO_2 + C_2O_4^{2-}} & \underline{\longrightarrow} & \underline{H_2O_2 + C_2O_4^-} \\ O_2 + 2H^+ + C_2O_4^{2-} & \longrightarrow & H_2O_2 + 2CO_2 \end{array}$$

Thus the net effect is that, for each molecule of oxalic acid which is oxidized by an induced air oxidation, the equivalent amount of hydrogen peroxide is formed. This of course reduces more permanganate.

In the titration of oxalic acid there are several sources of error, any of which may become significant if the working conditions are not selected with care.

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[46] G. E. Mapstone and J. W. Smith, *Chemistry & Industry*, 1952, 856.

[47] A. Richardson, *J. Chem. Soc.*, 65, 450 (1894); G. von Georgievics and L. Springer, *Monatsh.*, 21, 419 (1900); I. M. Kolthoff, *Z. anal. Chem.*, 64, 185 (1924).

[48] K. Schröder, *Z. öffentl. Chem.*, 16, 270, 290 (1910).

[49] E. Deiss, *Chem. Ztg.*, 50, 399 (1926); *Z. angew. Chem.*, 39, 664 (1926); cf. F. Oberhauser and W. Hensinger, *Ber.*, 61, 521 (1928); E. Schröer, *Ber.*, 69, 2037 (1936); K. Weber and A. Režek, *Ber.*, 70, 407 (1937).

[50] H. F. Launer, *J. Am. Chem. Soc.*, 55, 865 (1933).

[51] I. M. Kolthoff, unpublished; cf. V. A. Stenger, *Anal. Chem.*, 23, 1541 (1951)

1. Air-oxidation of the oxalic acid. According to Schröder[48] an atmospheric oxidation of oxalic acid is induced during permanganate titration, with formation of carbonic acid. Through addition of manganous sulfate or titanium dioxide the error can be minimized. McBride[52] did not regard it as serious in any event.

2. Formation of carbon monoxide. The reaction

$$H_2C_2O_4 \qquad\qquad CO_2 + CO + H_2O$$

is more likely to occur at higher temperatures and in the presence of manganese sulfate, according to Kolthoff.[47] Chromic ions also favor this autodecomposition of oxalic acid. Difficulty may be expected in the determination of any substance that requires prolonged heating with excess oxalic acid, such as pyrolusite or lead dioxide.

3. Loss of oxygen. It has already been mentioned that oxygen may be evolved from warm and acid solutions of permanganate. Both McBride and Kolthoff have noted oxygen losses, especially with rapid titration and insufficient stirring of the solution, or at higher acidity and greater dilution of the oxalic acid. According to Brasted,[53] however, there is no appreciable error due to the acid concentration even in $8N$ sulfuric acid.

4. Impurities in the water or acid. These factors have been discussed in Section 2; especially when the permanganate is to be used in excess does it become mandatory to make purity tests.

5. Abnormal oxidation products. McBride attributed an error to the formation of hydrogen peroxide, but this does not seem to occur. If, for example, hydrogen peroxide were formed by the mechanism of Deiss (p. 50), it would react further with permanganate and the net consumption of oxidant would be unaffected.

6. Presence of hydrochloric acid. According to Gooch and Peters[54] a reaction between permanganate and hydrochloric acid (or chloride ions) is induced by the permanganate-oxalic acid reaction. Addition of manganous salt prevents the formation of free chlorine or hypochlorous acid and eliminates the error. Baxter and Zanetti[55] noted that the initial temperature should be above 70 °C., and this was confirmed by Kolthoff. The effect of chloride is considered further on p. 104.

From the above it follows that the titration of oxalic acid, and therefore the standardization of permanganate against this compound, can give accurate results only when it is carried out under the optimum conditions. In a precision study Fowler and Bright[56] found that the time-honored procedure of McBride[52] gives a permanganate titer which may be 0.4 per cent too high, while the precision is not better than to 0.1 per cent. They recommended the following procedure, which yielded results agreeing with those obtained by the arsenic trioxide method.

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[52] R. S. McBride, *J. Am. Chem. Soc.*, 34, 393 (1912).

[53] R. C. Brasted, *Anal. Chem.*, 25, 673 (1953).

[54] F. A. Gooch and C. A. Peters, *Am. J. Sci.*, 7, 461 (1899); *Z. anorg. Chem.*, 21, 185 (1899).

[55] G. P. Baxter and J. E. Zanetti, *Am. Chem. J.*, 33, 500 (1905).

Procedure of Fowler and Bright: Dry a portion of the purified sodium oxalate (p. 48) at 105°C. and transfer about 0.3 g., accurately weighed, to a 600 ml. beaker. Add 250 ml. of 1:19 sulfuric acid which has previously been boiled for 10–15 minutes and cooled to 27 ± 3°C. Stir until the oxalate is dissolved, and introduce 39–40 ml. of $0.1N$ permanganate from the burette at a rate of 25–30 ml. per minute. Let stand until the pink color disappears, this generally taking about 45 seconds. (If too much permanganate has been added, a fresh start should be made.) Warm to between 55 and 60°C. and complete the titration to a faint pink that persists for 30 seconds. The last 0.5 ml. or so should be added dropwise, with care to obtain complete reduction of each drop before adding another. Determine the end-point correction in a blank experiment (generally 0.03–0.05 ml. of $0.1N$ solution) and subtract it from the observed titration.

Notes: (1) Kolthoff, Laitinen, and Lingane[57] have compared the normalities of $0.1N$ permanganate solution obtained by the methods of Fowler and Bright,[56] McBride,[52] and Kolthoff.[58] Assuming that the true normality of the permanganate was given by potentiometric titration against potassium iodide, and basing the oxalate calculations on 99.96 per cent purity for Bureau of Standards sodium oxalate, they determined the average errors of the three procedures to be as follows: Fowler and Bright, +0.07 ± 0.03 per cent; Kolthoff, +0.13 ± 0.09 per cent; McBride, +0.21 ± 0.1 per cent.

(2) The principal manipulative differences between these three procedures lie in the temperature maintained during titration. Kolthoff's directions called for heating the acidified solution to 75–85°C. before titrating.

(3) In the standardization of $0.01N$ permanganate the errors are correspondingly greater, amounting to 0.3–0.5 per cents by Kolthoff's method. At this dilution the titration error is pronounced; it can be decreased considerably by cooling the solution at the end-point, adding potassium iodide, and titrating the liberated iodine with $0.01N$ thiosulfate.

Potassium Ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$; equivalent weight, 422.39; rational, 422.20): Long ago de Haen[59] employed potassium ferrocyanide as a standard substance. It has the advantage of a high reaction weight but suffers from the fact that the end-point is not sharp. On this account, standardization by the potentiometric method[60] is to be preferred. The material is easily obtained pure by recrystallization and good products are commercially available.

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[56] R. M. Fowler and H. A. Bright, *J. Research Natl. Bur. Standards*, **15**, 493 (1935).

[57] I. M. Kolthoff, H. A. Laitinen, and J. J. Lingane, *J. Am. Chem. Soc.*, **59**, 429 (1937). See also R. E. Duggan, *J. Assoc. Offic. Agr. Chemists*, **28**, 596 (1945); **31**, 568 (1948).

[58] I. M. Kolthoff, *Z. anal. Chem.*, **64**, 185 (1924).

[59] E. de Haen, *Ann.*, **90**, 160 (1854).

Preparation: Crystallize commercial potassium ferrocyanide two or three times from water and dry to constant weight over deliquescent calcium chloride. The moisture content, determined by drying at 100°C., should be 12.80 per cent. Since the anhydrous salt can be prepared so readily in this way, it may be preferable to the trihydrate.

Standardization of Permanganate: If the solution is not acid enough or if it is not sufficiently diluted, a precipitate of potassium manganese ferrocyanide may form during titration. This substance is oxidized only slowly (see p. 89). Kolthoff obtained good results as follows: A weighed amount of potassium ferrocyanide is dissolved in $1N$ sulfuric acid, 120 ml. being allowed for 1 g. of the salt, and the solution is titrated with permanganate until the yellow ferricyanide color shows a tinge of orange. The end-point can be recognized within 0.1 per cent if for comparison one uses an already titrated solution to which a little ferrocyanide has been added.

Since the introduction of erioglaucine A and eriogreen B (cf. p. 25; also Vol. I, p. 138) as redox indicators in the determination of ferrocyanide,[61] the use of potassium ferrocyanide as a standard substance has assumed greater importance.

Procedure: The weighed amount of ferrocyanide, preferably not more than 1 g., is dissolved in 400 ml. of water containing 20 ml. of $8N$ sulfuric acid, treated with 1 ml. of 0.1 per cent erioglaucine or 2 ml. of 0.1 per cent eriogreen, and titrated with permanganate. Because of the color of the dissolved ions, the end-point change is from yellowish green to brownish orange with erioglaucine, or from deep yellow to orange yellow with eriogreen. The transition is sharp and can be observed well even under artificial illumination. If hydrochloric acid is used in place of sulfuric, some of the acid is oxidized and too much permanganate is consumed. The correction amounts to 0.10–0.15 ml. of $0.05N$ solution.

In place of the indicators mentioned, one can also use diphenylaminesulfonic acid, N-phenylanthranilic acid, or ferrous phenanthroline.

Note: According to Knop and Kubelková[62] potassium ferrocyanide is also well suited for the micro volumetric standardization of permanganate. However, since dilute ferrocyanide solution is light-sensitive the titration should be performed in moderately bright, diffuse daylight or, better still, in artificial light, immediately after preparation of the solution (within 15 minutes at the most). If one waits 2 hours, results about 0.5 per cent low will be obtained in titrating with $0.005N$ permanganate.

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[60] G. L. Kelley and R. T. Bohn, *J. Am. Chem. Soc.*, **41**, 1776 (1919); E. Müller and H. Lauterbach, *Z. anal. Chem.*, **61**, 398 (1922); I. M. Kolthoff, *Rec. trav. chim.*, **41**, 343 (1922).

[61] J. Knop, *Z. anal. Chem.*, **77**, 111 (1929).

[62] J. Knop and O. Kubelková, *Z. anal. Chem.*, **100**, 161 (1935).

To 1.00 ml. of $0.01N$ ferrocyanide are added 5 ml. of $4N$ sulfuric acid and 0.05–0.1 ml. of erioglaucine *A*. In titrating with $0.005N$ permanganate Knop and Kubelková found the titration error to be negligible. de Beer and Hjort,[63] however, reported that 0.05 ml. of 0.1 per cent indicator requires 0.012 ml. of $0.01N$ permanganate. The final volume of solution should not exceed 50 ml. and the sulfuric acid concentration should lie between 0.1 and $1.0N$.

Iron (Fe; atomic weight and rational weight, 55.85): When pure iron is dissolved in dilute sulfuric acid there is produced ferrous sulfate, which can easily be titrated with permanganate. This method of standardization has lost favor, however, because of the precautions required to prevent aerial oxidation of the solution and the difficulty of securing pure iron. Nevertheless, Fowler and Bright,[56] working with iron of 99.98 per cent purity prepared in the Metallurgy Division of the National Bureau of Standards, were able to obtain excellent results in standardizing permanganate against iron as compared with sodium oxalate.

Formerly it was customary to use fine, soft iron wire (piano wire), which before weighing was polished with emery cloth and then cleaned with writing paper or filter paper. Unfortunately this wire was never pure, containing generally 0.3 per cent or more of foreign substances. Furthermore, when it had once rusted, complete removal of rust was practically impossible, according to Kinder.[64] To allow for impurities in the wire, the iron content would be determined gravimetrically and a correction applied. According to Thiele and Deckert[65] and especially to Treadwell,[66] such a procedure is erroneous, for during solution of the wire other substances capable of consuming permanganate are formed from impurities in the wire (C, S, P, Si). The active strength may thus exceed 100 per cent, and, since the impurities behave differently under different conditions, the manner of dissolving the wire influences the result. Treadwell found effective strengths varying from 100.2 to 100.5 per cent for the same wire, depending upon the method employed.

Skrabal[67] eliminated the effect of carbides (and probably of several other impurities) by adding an excess of permanganate to the solution and allowing it to stand overnight in a warm place. After oxidation of the carbide in this way, the iron was reduced with stannous chloride and titrated by the Reinhardt-Zimmermann method (p. 84).

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[63] E. J. de Beer and A. M. Hjort, *Ind. Eng. Chem., Anal. Ed.*, 7, 120 (1935).

[64] H. Kinder, *Chem. Ztg.*, 30, 631 (1906); 31, 69, 117 (1907).

[65] H. Thiele and H. Deckert, *Z. angew. Chem.*, 14, 1233 (1901).

[66] F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Vol. II, 8th ed., Deuticke, Leipzig, 1919.

[67] A. Skrabal, *Z. anal. Chem.*, 42, 359 (1903).

Various attempts have been made to prepare entirely pure iron. Kinder[68] dissolved ingot iron in hydrochloric acid, oxidized it to ferric chloride, extracted with ether, evaporated, precipitated as sulfide, dissolved in sulfuric acid, and crystallized as ferrous sulfate. This he transposed with ammonium oxalate, the ferrous oxalate formed being dried, ignited to constant weight, and reduced in a stream of hydrogen. Classen[69] electrolyzed a solution of ferrous ammonium oxalate, but according to Avery and Dales[70] electrolytic iron always contains a small amount of carbon. Skrabal[67,71] obtained varying values (98.5–99.9 per cent) for the effective strength of iron prepared by Classen's method, although the carbon content amounted only to 0.06–0.20 per cent. He therefore worked out a different procedure for the electrolysis, using a cell voltage of 0.3–0.4. Unfortunately his report is not clear as to the permanganate titer obtained.

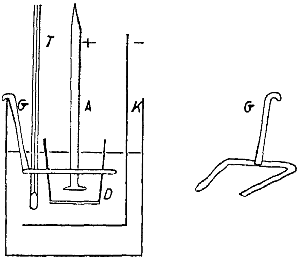

FIG. 2. Electrolysis apparatus of Moser and Schöninger.[72]

Moser and Schöninger[72] investigated anew the electrolytic preparation of iron and reported good results by the following procedure: A 200 ml. beaker (Fig. 2) serves as an electrolysis vessel, into which are placed 100 ml. of water, 3 or 4 g. of purest ferrous chloride, 12–15 g. of sodium chloride, 1 g. of boric acid, and 5 ml. of 4*N* hydrochloric acid. A disk (K) of platinum or tantalum, 6 cm. in diameter and supported by a wire of the same metal, serves as cathode; the anode (A) is an iron nail about 0.5 cm. thick, which is etched with nitric acid, rinsed with water, and placed head down in the bath. Between the two electrodes there is a diaphragm (D) consisting of a porous porcelain or glass filter crucible supported on a glass fork (G). The anode slime collects in the crucible and contamination of the electrolyte is thus avoided.

The cell is operated at 1.4–1.6 v. or enough to pass 0.3–0.4 ampere, giving a cathodic current density of 5–7 milliamperes per sq. cm. Electrolysis is allowed to proceed for 40 or 50 minutes at 60°C., whereby 0.15–0.20 g. of iron is deposited on the cathode. The latter is then removed from the solution before the current is turned off and is rinsed with water, dipped for several seconds in 0.1N potassium hydroxide, and washed in running water. The water is displaced by alcohol and the alcohol is evaporated in a gentle stream of dry air. After standing for 15 minutes in a desiccator, the electrode is ready for weighing.

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[68] H. Kinder, *Stahl u. Eisen*, **30**, 411 (1910).

[69] A. Classen, *Z. anal. Chem.*, 42, 516 (1903).

[70] S. Avery and B. Dales, *Ber.*, 32, 64, 2233 (1899).

[71] A. Skrabal, *Z. anal. Chem.*, **43**, 97 (1904); cf. H. Verwer, *Chem. Ztg.*, 25, 792 (1901); G. Lunge, *Z. angew. Chem.*, 17, 265 (1904); A. Pfaff, *Z. Elektrochem.*, 15, 703 (1909).

[72] L. Moser and W. Schöninger, *Z. anal. Chem.*, **70**, 235 (1927).

In standardizing permanganate, an excess of 0.25N sulfuric acid is placed in a beaker and freed from air by bubbling with carbon dioxide. While the gas flow is continued, the electrode is immersed in the acid until all iron is dissolved; the process may be hastened by warming. Phosphoric acid is added, if necessary, and the solution is titrated with permanganate. Moser and Schöninger obtained theoretical results with their electrolytic iron.

Wesly[73] states that iron prepared by the carbonyl process is free from the impurities commonly present in ordinary iron, and recommends it for use as a standard substance.

Brandt[74] suggested the use of pure ferric oxide in the standardization of permanganate. This must be dissolved in hydrochloric acid, reduced, and titrated as in Skrabal's method.

Ferrous Ammonium Sulfate (Mohr's salt, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$; equivalent weight, 392.15; rational, 391.91): Against the advantage of a high reaction weight possessed by this double salt, there stands the disadvantage that it is generally impure. Various authors[75] have opposed its use as a primary standard. Kolthoff has occasionally found effective strengths of only 95–99 per cent on products that seemed to be pure. A useful standard cannot be prepared from ordinary ferrous sulfate and ammonium sulfate.

Manganese, zinc, lead, nickel, and magnesium are common impurities of ferrous sulfate, most of which cannot be removed by recrystallization or precipitation from alcohol because they form mixed crystals either with the simple sulfate or with Mohr's salt.[76] To prepare the latter, therefore, one must start with pure materials.[77] Fortunately, ferric ammonium sulfate can be purified readily by recrystallization. A solution of this compound is treated with hydrogen sulfide until no more ferric ion is detectable (which may require several days) and is then filtered. Ferrous ammonium sulfate is crystallized out after evaporation and cooling; it is recrystallized and finally dried to constant weight over deliquescent sodium bromide. A preparation of 99.97 per cent effective strength can be obtained.

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[73] W. Wesly, *Z. anal. Chem.*, **91**, 341 (1933).

[74] L. Brandt, *Stahl u. Eisen*, **30**, 1844 (1910); *Chem. Ztg.*, **40**, 605, 631 (1910); cf. E. Hintz, *Z. angew. Chem.*, **27**, 9 (1914).

[75] N. Gräger, *Z. anal. Chem.*, **6**, 209 (1867); J. Volhard, *Ann.*, **198**, 327 (1879); C. Meineke, *Z. öffentl. Chem.*, **4**, 444 (1898); A. Skrabal, *Z. anal. Chem.*, **43**, 97 (1904); H. Cantoni and M. Basadonna, *Ann. chim. anal. et chim. appl.*, **9**, 365 (1904); O. Hackl, *Chem. Ztg.*, **46**, 1065 (1922).

[76] I. M. Kolthoff, *Z. anal. Chem.*, **64**, 255 (1924).

[77] L. L. de Koninck, *Bull. soc. chim. Belges*, **23**, 222 (1909); D. Florentin, *Bull. soc. chim. France*, (4) **13**, 362 (1913).

A commercial product which has been proved free from impurities can be relied upon as pure if recrystallized and dried as above. However, the testing of Mohr's salt for impurities is not simple and the material cannot be considered an ideal primary standard. Yet, if the effective strength is known, Mohr's salt is preferable to iron wire for the standardization of permanganate. A weighed sample of the salt is dissolved in water containing sulfuric acid and is titrated with permanganate to the appearance of an orange color. Addition of phosphoric acid makes the end-point sharper. Phosphoric acid binds ferric ions as a colorless complex so that the change is from colorless to pink.

To avoid the unreliability of Mohr's salt as a standard, Gräger[78] proposed the use of ferrous sodium sulfate, $FeSO_4.Na_2SO_4.4H_2O$, which is said to withstand drying at 100 °C. and to be stable in air. This salt has not come into general use.

Meineke[79] recommended ferric ammonium sulfate in place of the ferrous compound, since it is easily purified by crystallization. A disadvantage is its susceptibility to efflorescence even at 60 per cent relative humidity, although it is stable at 70 per cent. Before titration it must be reduced, for which several methods are available (p. 83). Considering the number of other, more attractive substances that are useful as standards, ferric alum has little practical importance.

Silver (Ag; equivalent and rational weight, 107.88): According to Tananaeff[80] metallic silver can be used for standardizing permanganate. It is dissolved in ferric alum solution and the reduced iron is titrated:

$$Fe^{3+} + Ag \longrightarrow Fe^{2+} + Ag^{+}$$

Because the reaction is reversible,[81] a generous excess of ferric alum must be present to dissolve all the silver.

Either powdered silver or silver foil may be used. Tananaeff[82] recommended a very reactive product which he prepared by electrolyzing a 1 per cent silver nitrate solution, acidified with 50 ml. of 1 :4 nitric acid per liter, at about 4.5 v. and 0.5–0.7 amp. The spongy metal was washed with water and dried to constant weight over phosphorus pentoxide.

Procedure for Standardization: Dissolve 5–10 g. of finely powdered ferric ammonium sulfate in 100 ml. of 4*N* sulfuric acid in a 250 ml. Erlenmeyer flask. Saturate the solution with carbon dioxide and then without stopping the flow of gas add about 0.3 g. of silver, accurately weighed. The optimum conditions for dissolving the metal are somewhat different for powder and for foil. With powder the solution should be cool at the beginning, but with foil it should be heated at once. The silver powder is shaken into the flask from a watch glass, which is rinsed off with water saturated with carbon dioxide. Most of the powder dissolves in the cool solution upon swirling the flask, but the solution remains turbid until the last traces are dissolved by warming. The whole procedure takes from 15 to 25 minutes.

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[78] N. Gräger, *Neues Jahrb. Pharm.*, **37**, 129 (1872); E. Biltz, *Z. anal. Chem.*, **13**, 124 (1874).

[79] C. Meineke, *Z. öffentl. Chem.*, **4**, 444 (1898).

[80] N. A. Tananaeff, *Z. anorg. u. allgem. Chem.*, **136**, 193 (1924); cf. K. Hopfgartner, *Monatsh.*, **26**, 469 (1905).

[81] For the equilibrium constant and earlier literature references, see N. A. Tananaeff, *Z. physik. Chem.*, **114**, 50 (1924).

[82] N. A. Tananaeff, *Chem. Ztg.*, **32**, 385 (1908).

When the solution is clear, increase the carbon dioxide stream and cool the flask in cold water. Add 15 ml. of 85 per cent phosphoric acid and titrate with permanganate. Tananaeff reported the results to be very accurate.

Potassium Stannous Chloride ($K_2SnCl_4 \cdot 2H_2O$; equivalent weight, 187.37; rational, 187.30): Karantassis and Capatos[83] state that potassium stannous chloride dihydrate is easy to prepare in pure form and is well suited for the standardization of permanganate and iodine. However, a stannous solution is very susceptible to air-oxidation and must be kept in an inert atmosphere.

Preparation of the Double Salt: Dissolve 14.9 g. of stannous chloride in water and enough hydrochloric acid to give a clear solution. To this add 15.5 g. of potassium chloride in the form of a saturated aqueous solution. Heat the mixture for some time on a water bath and allow it to cool very slowly. The monohydrate will form if the cooling is rapid. Filter out the white crystals and recrystallize from warm hydrochloric acid, then dry in air. The dihydrate is stable in air at room temperature and somewhat higher, losing its water of crystallization only near 100°C.

Procedure for Standardization: To 200 ml. of water add 2 g. of sodium bicarbonate and 20 ml. of conc. hydrochloric acid. Introduce a weighed quantity of the double salt, 0.4–0.5 g., bubble carbon dioxide through the solution and titrate with permanganate to a pink color.

Ferrous Ethylenediamine Sulfate ($FeC_2H_4(NH_3)_2(SO_4)_2$; equivalent weight, 382.15; rational, 381.91): Caraway and Oesper[84] described the preparation of ferrous ethylenediamine sulfate tetrahydrate and recommended it as a standard substance for permanganate, ceric sulfate, and dichromate solutions. It has the advantage of being quite stable under ordinary conditions, and it gives consistent results in titrations with the above-mentioned oxidants. Unfortunately the analysis given by the authors indicates an iron content of 14.66 per cent against a theoretical value of 14.62 per cent; they did not state which value was used in their calculations. Further tests should be carried out with weight burette technique before the material can be accepted as a primary standard. Singh and Singh,[85] however, have recommended a standard solution in place of ferrous ammonium sulfate for the indirect determination of several oxidizing agents; standard permanganate or dichromate is used for the titration of the excess of ferrous ethylenediamine sulfate.

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[83] T. Karantassis and L. Capatos, *Compt. rend.*, 194, 1938 (1932).

[84] K. P. Caraway and R. E. Oesper, *J. Chem. Educ.*, 24, 235 (1947); cf. H. Grossmann and B. Schück, *Z. anorg. Chem.*, 50, 26 (1906).

[85] B. Singh and S. Singh, *Anal. Chim. Acta*, 13, 222 (1955).

Antimony Metal (Sb; atomic weight, 121.76; rational, 121.755): Fiala[86] considers that metallic antimony is superior to other substances which have been recommended for standardization, for it is readily obtained in a pure state, it is not hygroscopic, and the titration can be done at room temperature.

Procedure: Weigh about 50 mg. of the powdered metal, dissolve in 3 ml. of concentrated sulfuric acid, and warm to promote the dissolution. Cool, dilute to 40 ml. with water, add 2.5 ml. of concentrated hydrochloric acid, and titrate with permanganate to the first rose tint which is stable for 1 minute.

Various other methods for standardizing permanganate solutions have been described in the literature but have not met with favor. Reference may be made to the gas-volumetric (nitrometer) method of Lunge[87] in which one measures the oxygen liberated by reduction of permanganate with hydrogen peroxide in acid solution. In general it is preferable to use a method more nearly similar to the use for which the permanganate is intended.

In conclusion, arsenic trioxide and sodium oxalate can be generally recommended as primary standards for use in practical analysis. Both are available from the National Bureau of Standards in highly purified form. Secondary standards of high equivalent weight may be useful if they are homogeneous and if their apparent equivalent weights have been determined by precise comparison with recognized primary standards.

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[86] R. Fiala, *Österr. Chem. Ztg.*, 50, 242 (1949).

[87] G. Lunge, *Ber.*, 18, 1872 (1885); *Z. angew. Chem.*, 3, 6 (1890); 17, 265 (1904). cf. p. 233.

CHAPTER III

OXIDIMETRY WITH PERMANGANATE

1. **Methods for Inorganic Substances.** *Iodide:* In acid solution iodide is oxidized to free iodine by permanganate. Titration to a visual end-point is impossible, however, unless one resorts to some method of eliminating the iodine color. The procedures of Lang, Andrews, and Berg, already described for the standardization of permanganate against potassium iodide, are all useful for titrating iodide in the absence of interfering ions. Lang's method (pp. 46 and 454), in which the iodide is oxidized to colorless iodine cyanide, is especially to be recommended. Either hydrochloric or sulfuric acid may be used for acidifying the solution. Unfortunately, bromide interferes seriously, being converted in part to cyanogen bromide, which reacts only slowly with iodide.

Earlier procedures involving extraction of iodine by shaking with benzene, carbon tetrachloride, or other solvents[1] have not much to commend them. A scheme that is essentially a modification of Andrews' method was proposed by Gorbatscheff and Kassatkina.[2] They saturated the iodide solution with sodium chloride, acidified, and titrated with permanganate. Chloroform serves as indicator, being colored red-violet by free iodine until the latter is converted to iodine chloride at the end-point. It is claimed that bromide (in small amounts ?) does not interfere, but complete details and supporting data are lacking.

As will be seen later, iodide in the presence of bromide can be determined more satisfactorily iodometrically (p. 248) or with hypochlorite (p. 586) than with permanganate.

In neutral or alkaline medium permanganate converts iodide to iodate:

$$KI + 2KMnO_4 + H_2O \longrightarrow KIO_3 + 2MnO_2 + 2KOH$$

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[1] See, for example, F. L. Hahn and H. Wolf, *Chem. Ztg.*, **50**, 674 (1926).

[2] S. W. Gorbatscheff and I. A. Kassatkina, *Z. anorg. u. allgem. Chem.*, **191**, 104 (1930).

The reaction can be applied in various ways[3] but is not of much practical importance. In an alkaline solution containing barium, however, iodide is oxidized to periodate[4] (cf. p. 35):

$$I^- + 8MnO_4 + 8Ba^{2+} + 8OH^- \longrightarrow IO_4^- + 8BaMnO_4 + 8K^+ + 4H_2O$$

One milliliter of $0.1M$ permanganate corresponds to 1.587 mg. of iodine.

Procedure: Place 1.5 g. of sodium hydroxide (free from organic matter) and 5 ml. of water in a 300 ml. flask, allow the alkali to dissolve, and cool the solution. Pipette in 20 ml. of $0.1M$ permanganate and then 10 ml. of the sample, which should be approximately $0.0125M$ in iodide. Mix, let stand for a minute, and add 5–7 ml. of saturated barium chloride solution; then back-titrate the excess permanganate with $0.05M$ sodium formate. If a significant amount of dark green barium manganate precipitates, introduce 10 drops of 1 per cent nickel nitrate solution as a catalyst and carry out the formate titration slowly, with thorough shaking. At the end-point the permanganate color disappears completely. Standardize the formate solution against the permanganate under similar conditions.

Note: Bromide does not interfere. Iodate may be determined in the same way as iodide, starting with 10 ml. of $0.05M$ solution.

Bromide: If permanganate solution is added dropwise to a hot bromide solution acidified with sulfuric acid and the liberated bromine is expelled by vigorous boiling, completion of the reaction can be recognized by appearance of the permanganate color. Winkler[5] made use of this fact for determining bromide. Since no interference is caused by 20 mg. or less of chloride per 100 ml., the procedure can be applied to the assay of commercial bromides.

Procedure: Place 0.2 g. of the alkali bromide in a 200 ml. wide-mouth Erlenmeyer flask with 100 ml. of water and 10 ml. of concentrated sulfuric acid. Add a little pumice powder or some boiling chips and heat the flask over a free flame. Keep at a vigorous boil and titrate slowly with permanganate until no more bromine is liberated and the solution assumes a pink color that remains for a minute or two.

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[3] L. Péan de St. Gilles, *Compt. rend.*, **46**, 624 (1858); C. Weltzien, *Ann.*, **120**, 349 (1861); W. Reinige, *Z. anal. Chem.*, **9**, 39 (1870); G. Klemp, *ibid.*, 20, 248 (1881); M. Gröger, *Z. angew. Chem.*, **7**, 52 (1894); H. Kiliani, *Chem. Ztg.*, **32**, 1018 (1908); A. Schwicker, *Z. anal. Chem.*, 110, 180 (1937).

[4] H. Stamm, *Z. angew. Chem.*, **47**, 791 (1934).

[5] L. W. Winkler, *Pharm. Zentralhalle*, **65**, 37 (1924); cf. *Z. angew. Chem.*, **28**, 477 (1915), and *Ausgewahlte Untersuchungsverfahren für das Laboratorium*, Enke, Stuttgart, 1931, p. 61.

Notes: (1) If the solution contains ammonium salts, ammonia should be expelled by boiling with alkali before titration. Iodide and other reducing agents interfere and should be absent.

(2) For the analysis of chloride-containing samples such as ocean water and mineral brines or salts, Winkler gives a distillation procedure. His 1915 article[5] should be consulted for details. The authors prefer the iodometric method (p. 254) for this case, since no preliminary distillation is required.

Hydrogen Sulfide: Free hydrogen sulfide reacts with permanganate in various ways. According to Hönig and Zatzek,[6] virtually complete oxidation to sulfate takes place in a boiling, alkaline solution, with formation of manganese dioxide; sulfate, tetrathionate, and sulfur are all formed at lower temperatures. St. Gilles,[7] on the other hand, believed that quantitative oxidation would not take place under any condition. Kolthoff[8] confirmed that, while oxidation is incomplete in acid or neutral medium, it is quantitative in alkaline solution:

$$S^{2-} + 2O_2 \qquad SO_4^{2-}$$

Procedure: To 25 ml. of 0.1*N* permanganate add 5–10 ml. of 4*N* sodium hydroxide and 10 ml. of approximately 0.1*N* (0.0125*M*) sulfide solution. Determine the excess of permanganate after 5 minutes by acidifying, adding potassium iodide, and titrating the liberated iodine with 0.1*N* thiosulfate.

Sulfurous Acid and Sulfites: According to St. Gilles,[7] oxidation with permanganate in acid solution leads to sulfuric and dithionic acids. Fordos and Gélis[9] recognized that the quantity of dithionic acid formed depends upon the acid concentration and temperature. Hönig and Zatzek,[6] as well as Pinnow,[10] found the oxidation of sulfurous acid to be incomplete in acid solution but practically quantitative in the presence of alkali.

The procedure is the same as for sulfide determination; a 2 minute reaction period is sufficient. Kolthoff[8] obtained results low by about 2 per cent in neutral solution, and 3–4 per cent in acid solutions.

Alsterberg[11] determined sulfurous acid by a different method. An excess of iodine cyanide is added to the weakly acid solution:

$$H_2SO_3 + ICN + H_2O \longrightarrow H_2SO_4 + HI + HCN$$

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[6] M. Hönig and E. Zatzek, *Monatsh.*, 4, 738 (1883).

[7] L. Péan de St. Gilles, *Ann. chim. et phys.*, 55, 381 (1859); cf. S. Mohammad and S. N. Bedi, *J. Indian Chem. Soc.*, 21, 55 (1944).

[8] I. M. Kolthoff, *Pharm. Weekblad*, 61, 841 (1924).

[9] J. Fordos and A. Gélis, *J. pharm. chim.*, 36, 113 (1859).

[10] J. Pinnow, *Z. anal. Chem.*, 43, 91 (1904); J. Milbauer, *ibid.*, 48, 17 (1909).

[11] G. Alsterberg, *Biochem. Z.*, 172, 224 (1926).

The liberated hydriodic acid is then titrated with permanganate in the presence of potassium cyanide and sulfuric acid, according to the procedure of Lang (p. 46).

Thiosulfate: St. Gilles[7] reported the formation of both dithionic and sulfuric acids from oxidation of thiosulfate in acid medium, whereas Dobbin[12] found tetrathionic acid also. Hönig and Zatzek[6, 13] obtained incomplete oxidation with permanganate in acetic acid solution, even after prolonged boiling. However, various workers[14] were able to secure stoichiometric conversion to sulfate by oxidation with alkaline permanganate:

$$S_2O_3^{2-} + 2O_2 + 2OH^- \longrightarrow 2SO_4^{2-} + H_2O$$

In this reaction, the equivalent weight of sodium thiosulfate is one eighth of its molecular weight. The procedure is the same as for hydrogen sulfide, with a waiting period of 2 minutes.

The above-mentioned reactions of sulfite and thiosulfate can be applied to the determination of both in a mixture. Both are oxidized with permanganate in alkaline solution, requiring 2 and 8 equivalents of oxidant per mole respectively. Against iodine, sulfite behaves in the same way, whereas thiosulfate is oxidized to tetrathionate with the consumption of only 1 equivalent of iodine per mole. The difference between the two titers, therefore, represents seven eighths of the permanganate titer of thiosulfate alone.

Selenious and Tellurous Acids: These compounds are oxidized to selenates and tellurates by alkaline permanganate. Stamm and Goehring[15] developed the following method for determining selenite.

Procedure: Place exactly 50 ml. of approximately 0.1 *M* permanganate in a 1 liter Erlenmeyer flask along with 25 ml. of a 23–25 per cent sodium hydroxide solution (sp. gr. 1.26–1.28) prepared from pure alkali. Mix and introduce a volume of selenite solution estimated to contain 40–120 mg. of selenium. Mix again and allow to stand for 15 minutes, after which the solution should be violet or blue; a green color indicates an excess of selenite.

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[12] L. Dobbin, *J. Soc. Chem. Ind.*, **20**, 212 (1901).

[13] M. Hönig and E. Zatzek, *Monatsh.*, **7**, 48 (1886); M. Hönig, *ibid.*, **6**, 492 (1885); M. Gläser, *ibid.*, **7**, 651 (1886); C. Luckow, *Z. anal. Chem.*, **32**, 53 (1893).

[14] H. Kiliani, *Chem. Ztg.*, **32**, 1018 (1908); G. Lunge and J. H. Smith, *J. Soc. Chem. Ind.*, **2**, 463 (1883). G. Lunge and D. Segaller, *ibid.*, **19**, 221 (1900). Quantitative oxidations of sulfite, thiosulfate, and hyposulfite with permanganate at pH 10–13 were reported by T. Murooka, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **21**, 1150 (1942); *Chem. Abstr.*, **42**, 8709 (1948).

[15] H. Stamm and M. Goehring, *Z. anal. Chem.*, **120**, 230 (1940); cf. O. Tomíček, O. Pročke, and V. Pavelka, *Collection Czech Chem. Communs.*, **11**, 449 (1939).

Dilute with 500 ml. of pure (double-distilled) water, acidify with 25 ml. of 50 per cent sulfuric acid, and pipette in 50 ml. of an oxalic acid solution that is slightly stronger than $0.25M$. Finally add 25 ml. of 2 per cent manganous sulfate solution. Heat to 50°C. and titrate in the customary way with standard $0.02M$ ($0.10N$) permanganate.

Carry out a blank experiment under the same conditions. The difference in the amounts of $0.02M$ permanganate used for unknown and blank corresponds to the selenite present. One milliliter is equal to 5.548 mg. of SeO_2.

Note: Any substance which reacts with permanganate in either alkaline or acid medium will interfere. In this connection specific mention may be made of copper, nickel, cobalt, and silver salts, which promote the decomposition of alkaline permanganate.

Barabas and Cooper[16] state that Stamm's procedure for the determination of selenites is not very reproducible. They prefer to oxidize in an acid medium and to use a procedure based on that of Gooch and Clemons[17] which can be applied to selenium, selenites, or selenates.

Procedure 1. Selenium or Selenite: Transfer 1 g. of sample to a beaker and dissolve in 50 ml. of warm water (selenite) or in 20 ml. of a mixture of equal parts of water, nitric and sulfuric acids (selenium). In the latter case simmer the solution until all nitrogen oxides have been expelled and the solution becomes colorless. Cool and dilute to 500 ml. in a graduated flask. Run a 25 ml. (selenium) or 50 ml. (selenite) aliquot from a burette into a 250 ml. Erlenmeyer flask. Add 20 ml. of $18N$ sulfuric acid, 100 ml. of water, and 12 g. of disodium hydrogen phosphate. Stir until all the salt has dissolved. Add 20 ml. of $0.1N$ permanganate and allow to stand for 30 minutes. Titrate the excess with $0.1N$ ferrous ammonium sulfate solution and add *o*-phenanthroline indicator when the end-point is approached.

Procedure 2. Selenate: Dissolve in 15 ml. of warm $18N$ sulfuric acid, cool, dilute as above, and take a 25 ml. aliquot. Add 1 g. of hydroxylamine hydrochloride and boil until all the selenium is precipitated, dissolve it in the mixed acid, and complete the determination as for selenium. Standardize the permanganate against selenium of high purity.

Note: When tellurium is present it should be corrected for by treating the sample with sulfuric acid and volatilizing the selenium by fuming at high temperatures; the residual tellurium is then titrated. Alternatively Schrenk and Browning's[17] dichromate method may be used.

Thiocyanate: Permanganate in the presence of acid oxidizes thiocyanic acid according to the equation:

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[16] S. Barabas and W. C. Cooper, *Anal. Chem.*, 28, 129 (1956); cf. I. M. Issa and R. M. Issa, *Chemist Analyst*, 45, 16 (1956).

[17] F. A. Gooch and C. F. Clemons, *Am. J. Sci.*, 50, 51 (1895); cf. W. T. Schrenk and B. L. Browning, *J. Am. Chem. Soc.*, 48, 2550 (1926).

$$HCNS + 3O + H_2O \longrightarrow HCN + H_2SO_4$$

From the abundant literature data,[18] and especially from the work of Schröder,[19] it appears that the permanganate consumption in acid solution is always too low. Induced oxidation by air appears to be the principal cause, but a small part of the thiocyanate may also be converted into a complex with manganese, which reacts only slowly with permanganate. The latter source of error may be eliminated by adding excess sodium carbonate near the end-point, to decompose the complex, and then acidifying again. Nevertheless the results will still be low because of oxygen interference and other causes.

Schröder recommended adding the thiocyanate to an excess of warm, acidified permanganate solution. Kolthoff arrived at the following procedure in unpublished experiments, but obtained results about 1 per cent low and did not recommend the method for exact analysis.

Procedure: Treat 50 ml. of $0.1N$ permanganate with 20 ml. of $4N$ sulfuric acid and warm to 50°C. Expel oxygen by adding three 0.2 g. portions of sodium bicarbonate, then pipette in 25 ml. of approximately $0.025M$ thiocyanate. Cool the solution, add an excess of potassium iodide, and titrate iodometrically.

Reinitzer and Pollet[20] believed that low results are due more to incomplete reaction and to dithionic acid formation than to air-oxidation; they described a modified method. It is doubtful whether this is more accurate than the other.

Procedure: Mix 20 or 25 ml. of $0.1N$ permanganate with 20 ml. of 1:1 sulfuric acid and warm to 60–70°C. Introduce the thiocyanate solution from a burette; when the color begins to fade, add thiocyanate dropwise with constant swirling until the solution has the faint pink tint of an ordinary permanganate end-point. Maintain the specified temperature throughout the titration.

Deshmukh and Joshi[21] state that the oxidation is quantitative in the presence of iodine monochloride.

Procedure: To 10 ml. of the thiocyanate solution contained in a bottle fitted with a ground-glass stopper (p. 45) add 10 ml. of iodine monochloride solution (see p. 44) and sufficient hydrochloric acid to make the normality 1.5–2*N*. Add carbon tetrachloride and titrate with permanganate, shaking vigorously between additions until the organic solvent becomes colorless.

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[18] F. W. Küster and A. Thiel, *Z. anorg. Chem.*, **35**, 43 (1903); S. W. Parr, *J. Am. Chem. Soc.*, **22**, 685 (1900); H. Grossmann and L. Hölter, *Chem. Ztg.*, **33**, 348 (1909); G. Masino, *ibid.*, **33**, 1173, 1185 (1909); W. Illarionow, *Z. anal. Chem.*, **87**, 26 (1932).

[19] K. Schröder, *Z. öffentl. Chem.*, **15**, 321 (1909); *Z. anal. Chem.*, **81**, 308 (1930).

[20] B. Reinitzer and H. Pollet, *Z. anal. Chem.*, **81**, 286 (1930).

[21] G. S. Deshmukh and M. K. Joshi, *Z. anal. Chem.*, **142**, 275 (1954).

Stamm[4] determines thiocyanate by oxidation with alkaline permanganate. The procedure is essentially the same as that described for iodide on p. 62, but see also the details given below for bismuth. One mole of thiocyanate requires 8 equivalents of oxidant:

$$\mathrm{KCNS} + 2\mathrm{O}_2 + 2\mathrm{KOH} \longrightarrow \mathrm{KCNO} + \mathrm{K}_2\mathrm{SO}_4 + \mathrm{H}_2\mathrm{O}$$

Bismuth: Application of the thiocyanate titration to the determination of bismuth has been made by Stamm and Goehring.[22] Bismuth is precipitated as bismuth chromic thiocyanate, $\mathrm{BiCr(CNS)_6}$, according to the directions of Mahr,[23] and thiocyanate in the precipitate is titrated with permanganate. The method is quite sensitive, since 48 equivalents of permanganate are required per mole of bismuth.

Procedure: Prepare the sample to contain at least 5 mg. of bismuth, in a concentration of about 1 mg. per 5 ml. of 0.3–1.0*N* nitric or sulfuric acid, free from chloride. Precipitate at room temperature by adding an excess of 10 per cent potassium chromium thiocyanate solution (see Note) and allowing to stand with frequent stirring for 10 minutes after crystallization begins. Filter on a sintered-glass crucible of fine porosity and wash with water; it is not necessary to transfer all precipitate to the filter. Discard the filtrate and replace the suction flask by a clean one. Wash the precipitation beaker with 10 ml. of 0.5–1.0 per cent sodium hydroxide (pure) and transfer this to the filter, agitating the precipitate well with a glass rod. Filter off the liquid and treat the precipitate successively with 0.5–1.0 per cent sulfuric acid and sodium hydroxide in 10 ml. portions to remove all thiocyanate. Extraction is complete when a drop of 50 per cent sulfuric acid on the residue gives no red coloration. The suspension should be filtered only while alkaline, and the combined extracts should be made just basic to litmus paper.

Pipette 20 ml. of approximately 0.1*M* permanganate into a 500 ml. flask and add 10 ml. of sodium hydroxide solution (30 g. per 100 ml., free from reducing substances). To this add the thiocyanate extract, or an aliquot portion of it equivalent to about 5 mg. of bismuth. Let stand for 25–30 minutes, then dilute with water to 150–200 ml. and pour in 10 ml. of 1:1 sulfuric acid. From a pipette introduce exactly 20 ml. of about 0.27*M* oxalic acid and add also 10 ml. of 5 per cent manganous sulfate tetrahydrate solution. Heat to 50°C. and titrate the excess oxalic acid with 0.02*M* permanganate.

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[22] H. Stamm and M. Goehring, *Z. anal. Chem.*, **115**, 1 (1938).

[23] C. Mahr, *Z. anorg. u. allgem. Chem.*, 208, 313 (1932).

Run a blank on the same quantities of $0.1M$ permanganate and $0.27M$ oxalic acid, together with 150 ml. of water, 5 ml. of 1:1 sulfuric acid, and 10 ml. of manganous sulfate solution. Heat and titrate in the same way with $0.02M$ permanganate. Subtract the blank from the previous titration; each milliliter of $0.02M$ solution taken represents 0.726 mg. of CNS^- or 0.4354 mg. of bismuth. Good results are obtained if more than 1 mg. of bismuth is present.

Note: To prepare potassium chromic thiocyanate,[24] dissolve 30 g. of KCNS and 15 g. of $CrCl_3 \cdot 6H_2O$ in a minimum of water. Evaporate on a steam bath, take up the dry residue with absolute alcohol, concentrate strongly, and filter by suction, washing with a little ether. Dissolve in alcohol, filter out KCl, and evaporate the filtrate. $K_3Cr(CNS)_6$ separates in dark red crystals, easily soluble in water.

Cyanide: According to Stamm,[4] cyanide can be determined by means of his procedure for formate (p. 116) or for iodide (p. 62). It is oxidized quantitatively to cyanate:

$$KCN + 2KMnO_4 + 2KOH \longrightarrow KCNO + 2K_2MnO_4 + H_2O$$
$$CN^- + O \longrightarrow CNO^-$$

Ammonia: No quantitative oxidation of ammonia to nitrogen or nitrogen oxides is possible with permanganate, yet ammonium salts may cause interference in other oxidimetric determinations. In Kolthoff's experience,[25] acid solutions more dilute than $0.01N$ in ammonium ions cause no trouble, but at higher concentrations a little nitrate is produced. In alkaline medium there is some formation of nitrite at practically any concentration. From 0.5 to 20 ml. of $0.1N$ ammonium chloride solution, made alkaline and treated with 20 ml. of permanganate, consumed 1.5 ml. of $0.1N$ oxidant during 24 hours.

Hydrazine: Petersen[26] reported that in sulfuric acid solution permanganate oxidizes hydrazine partially to nitrogen, with formation of some ammonia also, so that 17 moles of hydrazine consumed 26 equivalents of oxidant. Kolthoff,[27] failing to confirm this, obtained a ratio of 5:16 at boiling temperature. He believed that quantitative oxidation to nitrogen could be brought about in warm hydrochloric acid solution, but Houpt, Sherk, and Browne[28] pointed out that no stoichiometric reaction of hydrazine with acid permanganate is possible since variable results are obtained according to the conditions employed. Kolthoff now agrees with this finding. Hydrazine may be determined better iodometrically, or with bromate or hypochlorite. In alkaline medium, however, permanganate converts hydrazine smoothly to nitrogen and water; the procedure is similar to that for sulfide, with a half-hour period before back-titration.

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[24] J. Roesler, *Ann.*, 141, 185 (1867).

[25] I. M. Kolthoff, *Pharm. Weekblad*, 61, 958 (1924).

[26] J. Petersen, *Z. anorg. Chem.*, 5, 1 (1894). See also U. Roberto and F. Roncali, *Chem. Zentr.*, 1904, II, 616; L. Medri, *Gazz. chim. ital.*, 36, I, 373 (1906); A. W. Browne and F. F. Shetterly, *J. Am. Chem. Soc.*, 31, 221 (1909).

[27] I. M. Kolthoff, *J. Am. Chem. Soc.*, 46, 2014 (1924).

[28] A. G. Houpt, K. W. Sherk, and A. W. Browne, *Ind. Eng. Chem., Anal. Ed.*, 7, 54 (1935).

Hydrazoic Acid. In acid medium there is no stoichiometric reaction between azide and permanganate.[29] Van der Meulen[30] found that complex manganese compounds with a valence state between 2 and 7 oxidize azides in acid medium smoothly and quantitatively:

$$2HN_3 + O \longrightarrow H_2O + 3N_2$$

Thus 1 ml. $0.1N$ permanganate is equivalent to 6.5 mg. of NaN_3. (See also titration with ceric cerium, p. 139.) In order to transform permanganate to lower valence complexes, van der Meulen uses a solution which is $1M$ in sulfuric, $1M$ in phosphoric acid, and $1M$ in manganous sulfate (manganous solution).

Procedure: To 5 ml. of the above manganous solution add 10 ml. of $5N$ sulfuric acid, 25 ml. of $0.1N$ permanganate, and, with shaking, 20 ml. of approximately $0.1N$ azide solution. Shake the closed flask after gas evolution has ceased, let stand for 5 minutes, and back-titrate the excess of permanganate iodometrically.

Nitrite: Permanganate in neutral or alkaline solution does not attack nitrite, but complete oxidation to nitrate can be made to take place in the presence of acid:

$$NO_2^- + O \longrightarrow NO_3^-$$

The older literature offers procedures in which diluted nitrite solution is acidified with sulfuric acid and titrated directly with permanganate. Toward the end the reaction velocity diminishes. No accurate results are likely, since some nitrous acid escapes and some is oxidized by air. St. Gilles[7] and Kubel[31] therefore treated a neutral or alkaline nitrite solution with excess permanganate, acidified, and titrated the excess. The following procedures are fairly satisfactory.

Procedure: To 25 ml. of $0.1N$ permanganate in a glass-stoppered Erlenmeyer flask add 10 ml. of about $0.05M$ nitrite solution and 5 ml. of $4N$ sulfuric acid. Stopper the flask, swirl frequently during 15 minutes, and determine the excess permanganate iodometrically. This method is particularly suitable for dilute solutions.

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[29] See e. g., F. Raschig, *Schwefel and Stickstoffstudien*, Verlag Chemie, 1924, pp. 205–212; also *Gmelins Handbuch, Stickstoff Systemnummer* 4.

[30] J. H. van der Meulen, *Rec. trav. chim.*, **67**, 600 (1948).

[31] W. Kubel, *J. prakt. Chem.*, **102**, 229 (1867); cf. F. Raschig, *Ber.*, **38**, 3911 (1905); R. W. Atkinson, *Pharm. J.*, **16**, 809 (1886); J. S. Laird and T. C. Simpson, *J. Am. Chem. Soc.*, **41**, 524 (1919).

Notes: (1) According to Raschig[29] a 2 minute time of waiting is sufficient. Results accurate to within 0.1 per cent were obtained by Cool and Yoe,[32] following Raschig's directions.
(2) When nitrite was determined after addition of nitric acid, Brasted[33] noted that accurate results could be obtained only if the nitric acid was pretreated with sulfamic acid or if it was freshly boiled. He was able to determine nitrite satisfactorily in solutions $8N$ in nitric acid.

Procedure of Lunge:[34] The nitrite solution is made up to a known volume and a portion of it is placed in a burette. In a beaker 25 ml. of $0.1N$ permanganate and 20 ml. of $4N$ sulfuric acid are mixed with 200–250 ml. of water. This is warmed to 40 °C. and titrated with the nitrite. Toward the end, when the permanganate is nearly gone, the nitrite must be added very slowly and with constant stirring.

Note: Kolthoff found that an error of 1–2 per cent could easily arise. Cool and Yoe,[32] however, were able to secure almost theoretical results (±0.1 per cent) with moderately slow to very slow titration. Deviations of up to 0.5 per cent were encountered when the titration was rapid.

Because of the low velocity of oxidation, part of the nitrous acid may be decomposed before it reacts with permanganate. Klemenc[35] sought to eliminate any loss by placing an excess of permanganate and sulfuric acid in a flask, partially evacuating, and washing the nitrite in with water. A vacuum of 100 mm. of mercury is recommended by Hoeg,[36] who also described suitable apparatus. According to Hoeg the mixture should be allowed to stand for 5 minutes, then warmed to 40° and titrated with oxalic acid. It should be noted that Hoeg calculated the excess of permanganate to within 1 ml.; a large back-titration with oxalic acid is not recommended.

Application to Cobaltinitrite Precipitates: Several workers have applied the permanganate–nitrite titration to the determination of potassium after precipitation with sodium cobaltinitrite.[37] The precipitate is assumed to be $K_2NaCo(NO_2)_6 \cdot H_2O$ but suffers variations in composition under different conditions of formation, particularly with respect to the sodium-ion concentration. The method must be regarded as empirical.

For cobalt determination conditions are more favorable. In the presence of acetic acid, cobalt is completely precipitated by a great excess of potassium nitrite. The mixture is allowed to stand for 12 hours or longer before filtration and washing with 2 per cent ammonium nitrate solution. An excess of permanganate and some 1:4 sulfuric acid are allowed to react with the precipitate and the solution is warmed to 50°C. The excess of permanganate is determined iodometrically after cooling. Under these conditions cobalt returns to the divalent form and 11 equivalents of permanganate are required per mole of cobalt. Details are given in a paper by Wassilieff.[38]

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[32] R. D. Cool and J. H. Yoe, *Ind. Eng. Chem., Anal. Ed.,* 5, 112 (1933).
[33] R. C. Brasted, *Anal. Chem.,* 23, 980 (1951).
[34] G. Lunge, *Z. angew. Chem.,* 4, 629 (1891); *Chem. Ztg.,* 26, 501 (1904).
[35] A. Klemenc, *Z. anal. Chem.,* 61, 448 (1922).
[36] F. A. Hoeg, *Z. anal. Chem.,* 71, 102 (1927).
[37] R. H. Adie and T. B. Wood, *J. Chem. Soc.,* 77, 1076 (1900); J. E. Schueler and R. P. Thomas, *Ind. Eng. Chem., Anal. Ed.,* 5, 163 (1933); cf. T. Dupuis *Anal. Chim. Acta,* 9, 493 (1953).

Hypophosphorous Acid: In acidified solution, hypophosphorous acid is oxidized only slowly to phosphoric acid by permanganate. Most workers heat the solution (either acid, neutral, or alkaline[39]) for some time with excess oxidant and then back-titrate. As was stated on p. 39, decomposition of permanganate under these conditions leads to erroneous results. Kolthoff[40] preferred to carry out the reaction at room temperature.

To 10 ml. of 0.1*N* (0.025*M*) hypophosphite add 25 ml. of 0.1*N* permanganate and 5 ml. of 4*N* sulfuric acid. Provide also two blank tests with acid permanganate, and water. Keep in stoppered flasks for 24 hours and back-titrate iodometrically.

Schwicker[41] was able to bring about oxidation in half an hour at 50°C. or in $1^1/_2$ hours at room temperature. In other respects his procedure is analogous to the above. He also mentioned that addition of 4–5 drops of 5 per cent ammonium molybdate solution increases the rate of oxidation markedly, but gave no supporting data.

Stamm[4] oxidizes hypophosphite to phosphate with alkaline permanganate. The procedure is the same as for iodide (p. 62). Heredia[42] reported good results with the method.

Phosphorous Acid: This acid also reacts slowly with permanganate. The cold oxidation procedure described for hypophosphorous acid gives good results here as well. A waiting period of 2 hours is sufficient for acid solutions. Stamm's alkaline treatment (see above) is considerably more rapid.

Arsenious Acid: The determination of arsenious acid has already been covered in connection with the standardization of permanganate against arsenic trioxide (p. 43). Because of the slow reaction when no catalyst is present, it is generally impractical to employ the older procedures.[43] Either osmium tetroxide (Gleu) or one of the forms of iodine (Lang, etc.) may be used as a catalyst. Gleu's method may be followed if the solution contains sulfuric acid, preferably 0.5–1N, and not more than a small amount of chloride. In the presence of hydrochloric acid, catalysis by iodine or iodine chloride is preferable.

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[38] A. A. Wassilieff, *Z. anal. Chem.*, 78, 439 (1929).

[39] D. Köszegi, *Z. anal. Chem.*, 68, 216 (1926); L. Zivy, *Bull. soc. chim. France*, 39, 496 (1926).

[40] I. M. Kolthoff, *Z. anal. Chem.*, 69, 36 (1926). Earlier literature is cited in this paper.

[41] A. Schwicker, *Z. anal. Chem.*, 110, 167 (1937).

[42] P. A. Heredia, *Arch. farm. y bioquím. Tucumán*, 3, 173 (1947); *Chem. Abstr.*, 42, 59 (1948).

The catalytic action of iodine can be explained by rapid occurrence of the consecutive reaction: (Mn(VII) first reacts rapidly with arsenite to give Mn(III)):

$$2Mn^{3+} + I^- + H_2O \longrightarrow 2Mn^{2+} + HOI + H^+$$
$$HOI + AsO_3^{3-} \longrightarrow I^- + AsO_4^{3-} + H^+$$

According to Lang[44] the best conditions for smooth functioning of the catalyst are a hydrogen-ion concentration of at least 0.5N and a chloride-ion concentration of at least 0.1N. Increase in the concentration of either one of these *alone* is permissible, so that strong sulfuric acid solutions of arsenious acid may be titrated if but little chloride is present whereas chloride may be high if the acid is dilute. Up to a hydrochloric acid concentration of 1.3N the titration proceeds smoothly in either direction. Titration of arsenite with permanganate is possible at higher concentrations, especially if the permanganate is added slowly, but the reverse titration fails.

Applications of the Arsenite Titration: Cantoni[45] has applied the arsenite-permanganate titration to determinations of manganese dioxide, lead dioxide, and minium (Pb_3O_4).

About 0.5 g. of *pyrolusite* is boiled with 100 ml. of 0.1N arsenite solution and 20 ml. of concentrated sulfuric acid until completely decomposed. The solution is cooled, diluted with 400 ml. of water, and treated with a trace of iodide or iodate, whereupon the excess of arsenite may be titrated with permanganate.

For the assay of *lead dioxide* or *minium,* 1–2 g. samples are used and the sulfuric acid specified above is replaced by 100 ml. of 10 per cent hydrochloric acid.

Lead: When an oxidation is performed with persulfate in an alkaline solution containing nickel, higher oxides of nickel which strongly increase the reaction rate are formed. Lang[46] showed that in this way manganese can be quantitatively oxidized to permanganate; Lang and Zwerina[47] based a method for lead on the same principle. Lead is transformed into the dioxide and reduced with an excess of arsenite, which is titrated back. The oxidation is not stoichiometric since the apparent reaction weight of lead is found to be 104.6 rather than the theoretical 103.6, but the deviation is constant and the empirical factor can be used.

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[43] A. Bussy, *Compt. rend.*, **24**, 774 (1847). Other literature references are given in the papers of W. T. Hall and C. E. Carlson, *J. Am. Chem. Soc.*, **45**, 1615 (1923), and I. M. Kolthoff, *Pharm. Weekblad,* **61**, 317 (1924). See J. Holluta, *Z. anorg. u. allgem. Chem.*, **168**, 361 (1928), for a discussion of the permanganate-arsenite reaction mechanism.

[44] R. Lang, *Z. anal. Chem.*, **85**, 176 (1931).

[45] O. Cantoni, *Ann. chim. appl.*, **16**, 439 (1926).

[46] R. Lang, *Z. anorg. u. allgem. Chem.*, **158**, 370 (1926).

[47] R. Lang and J. Zwerina, *Z. anal. Chem.*, **93**, 248 (1933).

Procedure: About 0.45 g. of lead as nitrate in 50 ml. of neutral solution, or as sulfate, is treated with 20–25 ml. of chloride-free 2.5*N* sodium hydroxide, 20 ml. of nickel nitrate solution (135 g. $Ni(NO_3)_2 \cdot 6H_2O$, low in cobalt, per liter), and 2 g. of ammonia-free potassium persulfate, dissolved in water. The mixture is shaken frequently during a period of 2 minutes. From 30 to 40 ml. of 1:1 nitric acid, previously boiled to expel lower oxides of nitrogen, is added at a rate of about 5 drops per second, best from a burette, after which an equal quantity is poured in rapidly. Two minutes more are allowed for decomposition of the nickelic oxide, then an excess of 0.1*N* arsenite is added to reduce all lead dioxide. Ten milliliters of 1:1 hydrochloric acid and 1 drop of 0.005*M* potassium iodate solution are added and the excess arsenite is titrated with 0.1*N* permanganate. Each milliliter of 0.1*N* arsenite oxidized corresponds to 10.46 mg. of lead.

Notes: (1) Copper, ferric iron, and zinc are said not to interfere, but in their presence the nickel solution should be added before the sodium hydroxide. Cobalt, bismuth, tin, and antimony interfere.

(2) Among the anions, acetate and sulfate are not objectionable. Halides interfere by being oxidized, while phosphate and arsenate prevent the complete oxidation of lead.

(3) Manganese is oxidized to permanganate in the procedure. Both manganese and lead may be determined by replacing the nitric acid called for above with 40 ml. of 5*N* sulfuric acid (added at a rate of 2 drops per second), and filtering on asbestos. Permanganate in the filtrate is titrated with arsenite, employing iodate catalysis, and lead dioxide on the filter is transferred to a porcelain dish and treated as before, except that 100 ml. of *N* hydrochloric acid is added after the excess of arsenite.

(4) Cerium can be oxidized in much the same way[48] and titrated with arsenite in the presence of iodide and manganous ion as catalysts, but the persulfate-ferrous method (p. 367) is to be preferred.

Antimony: In the presence of hydrochloric acid, trivalent antimony is oxidized directly to the pentavalent form by permanganate. The acidity is critical. If too little is present, some hydrolysis of antimony occurs, giving a low result; too strong acid leads to chlorine formation and a high titer.

Procedure:[49] Prepare the sample so that about 0.2 g. of antimonous oxide is dissolved completely in 25 ml. of concentrated hydrochloric acid (or in 20 ml. of hydrochloric and 10 ml. of sulfuric; Note 1) and dilute to 150 ml. with water. Cool to about 20°C. and titrate slowly but continuously with 0.1*N* permanganate to a faint pink that persists for 10–20 seconds. One milliliter corresponds to 6.089 mg. of Sb. If the antimony is originally pentavalent, it may be reduced with sulfur dioxide. The excess of the latter is expelled by boiling, but precautions should be taken to prevent small losses of antimony.

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[48] R. Lang and J. Zwerina, *Z. anal. Chem.*, 91, 5 (1932).

[49] Cf. W. M. McNabb and E. C. Wagner, *Ind. Eng. Chem., Anal. Ed.*, 2, 251 (1930); J. Knop, *Z. anal. Chem.*, **63**, 81 (1923); O. Collenberg and G. Bakke, *ibid.*, **63**, 229 (1923).

Notes: (1) According to Pugh[50] the optimum concentrations of sulfuric and hydrochloric acids are interdependent. For a total solution volume of 200 ml. he recommends the following quantities of concentrated acids:

H_2SO_4, ml.	0	10	20	30
HCl, ml.	30–50	30–35	15–20	10–15

(2) Before 1921 the titration was believed to be empirical because of an error in the atomic weight of antimony. After Willard and McAlpine[51] had demonstrated that the atomic weight is 121.77 rather than 120.2, the titration was shown by Knop and others to be stoichiometric within 0.1–0.2 per cent, under good conditions.

(3) An iodine monochloride end-point (p. 44) may be used[52] provided that the hydrochloric acid concentration is kept between 2.5 and $3N$. For a final volume of 100–150 ml., 5 ml. of $0.025M$ iodine monochloride and 5 ml. of carbon tetrachloride should be added.

(4) In the analysis of lead-antimony alloys, retention of antimony by precipitated lead sulfate may cause low results. Pugh[50,53] weighs out a sample containing about 0.1 g. of Sb and dissolves by heating with 20–50 ml. of sulfuric acid, depending upon the lead content. The mixture is cooled, diluted to 100 ml., and allowed to settle. The clear solution is decanted off and boiled for 5 minutes to expel sulfurous acid. Meanwhile the precipitate is boiled with 20–30 ml. of 1:1 hydrochloric acid. When all is dissolved, the two solutions are mixed, diluted to 200 ml., and titrated slowly at 40–60°C. Methyl orange serves as indicator, being decolorized at the end-point. Tin is converted to the stannic form during solution of the alloy and does not interfere.

(5) In the presence of 0.3 g. of telluric acid, antimony can be titrated potentiometrically in alkaline medium with permanganate. The manganese goes to a valence of 4 but does not precipitate as dioxide.[54]

Tin: Stannous tin is quantitatively oxidized to stannic by permanganate, but the titration must be carried out in an inert atmosphere to avoid induced air-oxidation of the bivalent tin (see Vol. I, pp. 162, 176). This can be avoided by treating the solution with an excess of ferric salt and titrating the ferrous iron that is formed. For most purposes, however, the iodometric method (p. 319) is to be preferred.

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[50] W. Pugh, *J. Chem. Soc.*, 136, 1 (1933).

[51] H. H. Willard and R. K. McAlpine, *J. Am. Chem. Soc.*, 43, 797 (1921).

[52] E. W. Hammock, R. A. Brown, and E. H. Swift, *Anal. Chem.*, 20, 1048 (1948).

[53] See also W. H. Low, *J. Am. Chem. Soc.*, 29, 66 (1907); L. I. Shaw, C. F. Whittemore, and T. H. Westby, *Ind. Eng. Chem., Anal. Ed.*, 2, 402 (1930); L. Silverman, *Chemist Analyst*, 33, 78 (1944); A. Wassilieff and H. Stutzer, *Z. anal. Chem.*, 78, 97 (1929); R. G. Myers, *Philippine J. Sci.*, 64, 365 (1937), 66, 75 (1938); *Chem. Abstr.*, 32, 6173, 8979 (1938).

[54] O. Tomíček, O. Pročke, and V. Pavelka, *Collection Czech Chem. Communs.*, 11, 449 (1939); cf. J. F. Norris and H. Fay, *Am. Chem. J.*, 20, 280 (1898); B. Brauner, *Z. anal. Chem.*, 55, 225 (1916).

Hydrogen Peroxide: In acid solution hydrogen peroxide reduces permanganate:

$$5H_2O_2 + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 5O_2 + 8H_2O$$
$$H_2O_2 + O \longrightarrow H_2O + O_2$$

The titration proceeds well in either sulfuric or hydrochloric acid solution at room temperature. As in the titration of oxalic acid, the reaction is slow at first; a manganous salt may be added as catalyst but is not essential.

Procedure:[55] Weigh out about 2 g. of 3 per cent hydrogen peroxide and rinse into a beaker containing 75–100 ml. of water and 10 ml. of 1:1 sulfuric acid. Titrate with $0.1N$ permanganate at a rate of 10–40 ml. per minute, to a faint but permanent pink. A fading end-point indicates the presence of organic matter.

Notes: (1) Working with weight burettes and using 10 g. samples, Huckaba and Keyes[55] obtained results in excellent agreement with those found by an oxygen evolution method which they developed.

(2) The procedure is not very accurate for peroxide that is stabilized with acetanilide or other organic material. For such samples the iodometric and cerimetric methods are better.

Peroxide in Presence of Persulfates: On account of their very slight hydrolysis, perdisulfuric acid (HO_3SOOSO_3H) and permonosulfuric acid ($HOOSO_3H$) react so slowly with permanganate that they cannot be titrated. It has been suggested[56] that peroxides may be determined roughly in the presence of persulfates by titrating rapidly and at great dilution. According to Friend,[57] however, an accurate determination is impossible because these substances react with one another:

$$K_2S_2O_8 + H_2O_2 \longrightarrow 2KHSO_4 + O_2$$

The reaction is catalyzed by manganese and also by silver. Van der Meulen[58] found relatively large errors in the titration, especially in the presence of a manganous salt. He recommends determining the sum of persulfate and peroxide by adding an excess of ferrous iron and back-titrating with permanganate. In another portion the peroxide is decomposed by addition of alkali and a trace of osmium tetroxide. The remaining persulfate is determined with ferrous iron and permanganate as before.

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[55] Cf. C. E. Huckaba and F. G. Keyes, *J. Am. Chem. Soc.*, **70**, 1640 (1948); J. S. Reichert, S. A. McNeight, and H. W. Rudel, *Ind. Eng. Chem., Anal. Ed.*, **11**, 194 (1939).

[56] A. Bayer and V. Villiger, *Ber.*, **33**, 2488 (1900); **34**, 853 (1901).

[57] J. A. N. Friend, *J. Chem. Soc.*, **85**, 597 (1904); **89**, 1092 (1906); *Proc. Chem. Soc.*, **20**, 198 (1904); cf. U. M. Nayak, *J. Indian Chem. Soc.*, **8**, 535 (1931).

[58] J. H. van der Meulen, *Rec. trav. chim.*, **58**, 553 (1939).

Unpublished experiments by Kolthoff and coworkers gave satisfactory results in the direct titration of a mixture of persulfate and hydrogen peroxide, when the permanganate was added rapidly. The approximate quantity of permanganate needed was determined in a preliminary titration, then this amount less about 3 per cent was added to a duplicate sample in 20–30 seconds and the titration was completed in the usual way. After the peroxide determination, the persulfate could be determined with ferrous sulfate. Results accurate to within 1 per cent could be obtained even in the presence of large amounts of manganous salt and under varying conditions. The titration can also be carried out with ceric sulfate.

Application to Other Inorganic Peroxides: Perborates, the alkali peroxides, and some of the alkaline earth peroxides can be determined in acid solution, in the same way as hydrogen peroxide. Barium peroxide, however, undergoes some decomposition when dissolved in hydrochloric acid. Wagner[59] found that addition of phosphoric acid prevents the error. This was confirmed by Scarlett,[60] who recommends using a solvent composed of 50 ml. of concentrated hydrochloric acid, 20 ml. of 85 per cent phosphoric acid, and a few crystals of manganous chloride, all diluted to 1 liter with water. From 0.4 to 0.8 g. of sample is added to 100–150 ml. of the solvent, stirred until dissolved, and titrated with 0.1*N* permanganate. Mattner[61] recommends dissolution of barium peroxide in perchloric acid. He dissolves 0.2–0.4 g. in 10–15 ml. of 15 per cent perchloric acid (any small residue being disregarded), adds a few drops of manganous sulfate solution, and titrates with permanganate. He claims that there is no loss of oxygen and that the results are higher than those obtained by the iodometric procedure.

Iron Compounds.* (*a*) *Ferrous Iron: The first permanganate titration proposed was that of ferrous iron, published in 1846 by Margueritte.[62] When the only acid present is sulfuric acid, almost no difficulty is encountered. The solution is colored faintly yellow by the ferric iron formed, and at the end-point it becomes orange with the first small excess of permanganate. In order to obtain a change from colorless to pink one adds phosphoric acid, which binds ferric iron in the form of a colorless complex.

During titration at room temperature there is no interference from dissolved oxygen, even in the presence of finely divided solid materials. At higher temperature there arises an induced oxidation error of

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[59] E. C. Wagner, *Ind. Eng. Chem.*, **17**, 972 (1925).

[60] A. J. Scarlett, *Chemist Analyst*, **30**, 57 (1941).

[61] J. Mattner, *Z. anal. Chem.*, **135**, 415 (1952).

[62] F. Margueritte, *Ann. chim. et phys.*, **18**, 244 (1846).

−0.3 to −0.4 per cent if one titrates slowly;[63] the error is increased somewhat in the presence of phosphoric acid but may be lowered to negligible proportions if the permanganate is run in quickly. Very dilute solutions can be titrated precisely, but a correction for the titration error should be applied.

Much has been written about the interfering effect of chloride ions in ferrous iron determinations. The question is of great practical importance in the analysis of ores and alloys which have to be dissolved in hydrochloric acid. Although Margueritte[62] had titrated cold, very dilute hydrochloric acid solutions, Löwenthal and Lenssen[64] recognized that under these conditions some oxidation to chlorine (or, more likely, to hypochlorous acid[65]) takes place. Fresenius[66] confirmed their finding but apparently did not realize the beneficial action of manganous ions. It was Kessler,[67] to whom we are indebted for a thorough study of the iron titration, who first explained the favorable effect of bivalent manganese. He found also, as Wagner,[68] Friend,[69] and Kolthoff confirmed, that even small amounts of hydrochloric acid interfere, and that the error grows larger with increasing dilution of the iron and with increasing titration velocity. This is illustrated in Table I.

TABLE I

Titration of Ferrous Sulfate–Hydrochloric Acid Solutions
(10 ml. of $4N$ HCl present in each case)

Ferrous sulfate	Titration rate	Error (%)
25 ml. of $0.1N$	Fast	+0.5
25 ml. of $0.1N$	Slow	+0.1
25 ml. of $0.01N$	Fast	+5.0
25 ml. of $0.01N$	Slow	+2.3

Zimmermann[70] concluded from the experiments of Fresenius[66] that manganous ion eliminates the chloride error, and he recommended that a manganous salt be added when chloride is present. Later Reinhardt[71] improved the procedure; the mixture which he described is still known as Reinhardt-Zimmermann solution.

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[63] I. M. Kolthoff and N. Smit, *Pharm. Weekblad,* 61, 1082 (1924).

[64] J. Löwenthal and E. Lenssen, *Z. anal. Chem.*, 1, 329 (1862).

[65] G. P. Baxter and H. L. Frevert, *Am. Chem. J.*, **34**, 109 (1905).

[66] R. Fresenius, *Z. anal. Chem.*, **1**, 361 (1862).

[67] F. Kessler, *Ann. Physik,* **118**, 17 (1863).

[68] J. Wagner, *Massanalytische Studien,* Dissertation, Leipzig, 1898, p. 78; *Z. physik. Chem.*, **28**, 33 (1899).

[69] J. A. N. Friend, *J. Chem. Soc.*, 95, 1228 (1909).

[70] C. Zimmermann, *Ann.*, **213**, 305 (1882).

The reagent consists of 67 g. of manganous sulfate tetrahydrate dissolved in 400–500 ml. of water, treated with 160 ml. of 85 per cent phosphoric acid (sp. gr. 1.7) and 133 ml. of concentrated sulfuric acid, and diluted to 1 liter with water. Reinhardt used 60 ml. for each determination.

Baxter and Frevert[65] established that at higher temperature manganese is not as effective (cf. p. 104); at 80°C. the error is 0.2–0.3 per cent. Kolthoff confirmed this for $0.1N$ solutions and observed that with tenfold dilution the error becomes much greater. Even at room temperature there is an overtitration of about 1 per cent in the case of $0.01N$ solutions treated with Reinhardt-Zimmermann reagent. An odor of chlorine or hypochlorous acid is noticeable.

An alternative to the Reinhardt-Zimmermann solution has been proposed by Somasundaram and Suryanarayana.[72] They examined a large number of reagents but very few proved suitable; sodium acetate and sodium borate were satisfactory in pure solution but were useless when applied to the analysis of iron ores. Manganous acetate gave good results but was unsatisfactory when more than 1.5 g. was required. They finally recommend addition of 25 ml. of a mixture of 30 per cent sodium sulfate and 30 per cent potassium fluoride in the ratio of 5:1, or 35 ml. of a mixture of 10 per cent potassium sulfate and 10 per cent sodium fluoride in the ratio of 6:1. This reagent is stated to be cheaper and more easily prepared than Reinhardt-Zimmermann solution and the end-points are sharper and less fleeting. If hydrochloric acid over and above that necessary to decompose the ore is present, the new reagent is less effective.

However, these authors appear to be unaware that Rose[73] mentioned the use of potassium fluoride and sulfate for inhibiting the reaction in 1871. According to Follenius,[74] this reagent has little effect.

A small quantity of permanganate alone does not oxidize hydrochloric acid in the cold and at the dilution commonly encountered in iron titrations, whereas a distinct chlorine odor arises if a little ferrous salt is added. Zimmerman[70] gave the following explanation for this induced reaction: ferrous iron reacts with the oxidant so energetically that there is formed a higher oxide.[75] The latter decomposes to ferric iron and oxygen, simultaneously attacking hydrochloric acid. This assumption is also met in the "primary oxide" theory of Manchot (Vol. I, p. 170). Manganous ion, if present, is presumed to serve as an oxygen carrier by first forming manganic oxide or hydrated peroxide, which then oxidizes the ferrous iron. In more modern terms, manganous ion lowers the oxidation potential of the system:[76]

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[71] C. Reinhardt, *Chem. Ztg.*, **13**, 323 (1889).

[72] K. M. Somasundaram and C. V. Suryanarayana, *Z. anorg. u. allgem. Chem.*, **227**, 181 (1954).

[73] H. Rose, *Handbuch der analytischen Chemie*, Braunschweig, vol. 2, 1871, p. 926.

[74] O. Follenius, *Z. anal. Chem.*, **11**, 177 (1872).

[75] Cf. A. Schleicher, *Z. anal. Chem.*, **144**, 100 (1955).

$$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$$

To summarize, it may be concluded from the results quoted above and from those of other workers[77] that the permanganate titration of ferrous iron proceeds most satisfactorily in sulfuric acid solution at room temperature. If chloride is present, the use of Reinhardt-Zimmermann solution is called for and the titration should be carried out slowly. Even these precautions fail to eliminate the chlorine error completely at higher temperatures or with solutions as dilute as $0.01N$. For accurate titrations of ferrous iron in the presence of hydrochloric acid, the use of ceric sulfate (p. 147) or potassium dichromate (p. 177) is recommended.

Use of Redox Indicators in Microtitrations: Knop and Kubelková[78] studied various dyes of the triarylmethane group for their usefulness in microdeterminations of iron. Among those found suitable were cyanin B, cyanol fast green 2G, erioglaucine A, eriogreen B, patent blue A, setocyanine O, setopaline, xylene blue AS, xylene blue VS, and xylene cyanol FF (see p. 25, and also Vol. I, p. 138). In the procedure, a ferrous solution containing about 1 mg of iron is treated with 5 ml. of $1N$ sulfuric or hydrochloric acid, 1–2 ml. of 10 per cent manganous sulfate solution, and 0.05–0.1 ml. of 0.1 per cent indicator. While the flask is swirled vigorously and continuously, $0.005N$ permanganate is run in dropwise but rapidly until the indicator changes color and remains in its new form for at least 10 seconds. Accuracy to within 0.1 per cent is reported if the permanganate is standardized against ferrous iron under identical conditions. The presence of relatively much manganous salt is necessary when hydrochloric acid is used, to inhibit chlorination of the indicator during titration. In determining as little as 0.1 mg. of iron, an indicator correction should be applied; an error of 0.3–0.5 per cent is to be expected.

(*b*) ***Reduction with Ferrous Sulfate:*** Many oxidizing agents can be determined by reducing with ferrous salts. If the reaction in

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[76] Cf. H. Schäfer, *Angew. Chem.*, **66**, 229 (1954).

[77] O. L. Barnebey, *J. Am. Chem. Soc.*, **36**, 1429 (1914); **37**, 1481 (1915); G. J. Hough, *ibid.*, **32**, 539 (1910); T. W. Harrison and F. M. Perkin, *Analyst*, **33**, 43 (1908); G. C. Jones and J. H. Jeffrey, *ibid.*, **34**, 306 (1909); R. Schwarz and B. Rolfes, *Chem. Ztg.*, **43**, 51 (1919); L. Brandt, *ibid.*, **43**, 373 (1919); **44**, 101, 121 (1920); W. Manchot, *Ann.*, **325**, 93, 105 (1902); A. Skrabal, *Z. anal. Chem.*, **42**, 359 (1903). According to Barnebey, hydrofluoric acid causes somewhat erratic results but its effect may be overcome by adding boric acid.

[78] J. Knop and O. Kubelková, *Z. anal. Chem.*, **85**, 401 (1931); **77**, 125 (1929); J. Knop, *ibid.*, **100**, 161 (1935).

Moskowitz (p. 183) found that the initial reduction could be catalyzed by molybdate ions, thus shortening the reaction time.

In a more recent study, Leithe[86] has cut the reaction time further by increasing the acidity and adding sodium chloride. He claims that air exclusion is unnecessary under these conditions; either dichromate or permanganate is used for the back-titration. The method is applied to the analysis of fertilizers and commercial products. Szabó and Bartha[87] carry out the reduction in alkaline medium using silver diammine sulfate as catalyst. When the reaction is complete, the solution is acidified and titrated with permanganate.

Vanadium and Chromium: Vanadium(V) and chromium(VI) can be determined by reducing with an excess of standard ferrous ammonium sulfate solution and titrating back with permanganate. The main applications of this titration are to the determination of vanadium and chromium in metals and ores. One of the oldest methods for the determination of chromium in steels, and which is still used widely, is that of Vignal.[88] The oxidation is effected with permanganate and the excess is destroyed by boiling with manganous sulfate. Manganese dioxide is produced and is filtered off. In another method, which is used extensively, the oxidation is achieved with ammonium persulfate in the presence of silver nitrate,[89] and the excess of oxidant is destroyed by boiling. If manganese is present, permanganate is formed but is reduced selectively with hydrochloric acid.

Many variations have been described and these should be sought in the appropriate textbooks of metallurgical analysis. In general, the variations lie in the method used for oxidizing the elements to the higher valency states or for destroying the excess of this oxidant.

Willard and Young[90] developed a rapid method for determining vanadium and chromium in steels that are free from tungsten (wolfram). By means of perchloric acid oxidation these elements are converted to vanadic and chromic acids, the sum of which can be found by adding excess ferrous sulfate and back-titrating with permanganate. 1,10-Phenanthroline serves as indicator for the end-point at which ferrous iron, but not vanadyl ion, is oxidized in M sulfuric acid. The acidity is then lowered with sodium acetate and the titration is continued in a warm solution. Under these conditions vanadyl ion goes to vanadate, the oxidation potential of the system being diminished markedly when hydrogen ions are removed:

$$VO^{2+} + 2H_2O \rightleftharpoons VO_3^- + 4H^+ + e$$

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[86] W. Leithe, *Anal. Chem.*, **20**, 1082 (1948).

[87] Z. G. Szabó and L. Bartha, *Acta Chim. Acad. Sci. Hung.*, **1**, 116 (1951); *Anal. Chim. Acta*, **5**, 33 (1951).

[88] H. Vignal, *Chem. News*, **53**, 195 (1886).

[89] H. E. Walters, *J. Am. Chem. Soc.*, **27**, 1550 (1905); M. Philips, *Stahl u. Eisen*, **27**, 1164 (1907).

[90] H. H. Willard and P. Young, *Ind. Eng. Chem., Anal. Ed.*, **6**, 48 (1934).

Procedure: Weigh out a sample varying from 0.25 g. for stainless steels to 2.0 g. for low chromium steels and oxidize with perchloric acid as described on p. 6. Dilute the cooled, chlorine-free solution to 250–300 ml. and add 15 ml. of 1:1 phosphoric acid. Measure in an excess of $0.1N$ ferrous sulfate, add 2–3 drops of $0.025M$ ferroin indicator, and titrate immediately with $0.05N$ permanganate to a change from pink to clear green, permanent for a minute or more. Next add sufficient crystallized sodium acetate to react with the free perchloric acid present. This may be calculated on the basis that 1 g of steel uses up 5.4 ml. of 70 per cent perchloric acid, and that each milliliter remaining requires 1.6 g. of the acetate. Heat the solution to 50 °C., using a thermometer as a stirring rod, and titrate the vanadyl salt at once with $0.05N$ permanganate. Because of the small quantities generally present and the slowness of the reaction, the reagent should be run in slowly. Addition of more indicator may be necessary, but the color change is the same as before. Standardize the ferrous solution by titrating 20 or 25 ml. of it in 250 ml. of solution containing 10–15 ml. of 70 per cent perchloric acid and 2 drops of indicator.

Note: For details of more recent methods several other papers should be consulted.[91]

Manganese; Permanganate: Permanganate may be determined easily by adding an excess of standard ferrous sulfate to the acidified solution and titrating back with standard permanganate. Manganese may be oxidized to permanganate by ozonization (p. 5) or periodate (p. 5) or bismuthate (p. 4). The final titration is generally taken to the permanganate color.

(*c*) ***Ferric Iron:*** In order to determine ferric iron (or total iron in a mixture of ferric and ferrous) by titration with permanganate or other oxidant, the iron must first be reduced to the ferrous state. Methods for carrying out the reduction with various reagents, such as metals, hydrogen sulfide, and sulfur dioxide, are described in Chapter I. When the excess of reducing agent can be removed completely and no interfering substances are present, the ferrous iron can be titrated directly with permanganate according to the procedure on p. 76. Some methods applicable to other cases are given below. Generally it is preferable to titrate with permanganate when the only acids present are sulfuric and phosphoric, or sulfuric alone, but hydrochloric acid is permissible if preventive solution is to be added and is indeed desirable when stannous chloride is used as the

[91] K. Merz and M. Schnabel, *Metallurgie*, 5, 163 (1955); W. Furness, *Analyst*, 75, 2 (1950); T. Kitamura, *Japan Analyst*, 3, 329 (1954); B. P. Shlyapin, *Zavodskaya Lab.*, 16, 1661 (1950).

reducing agent. Nitric acid is objectionable in any event and should be expelled by heating to dense fumes of sulfuric acid.

Stannous Chloride Method (cf. p. 10). The reagents required are (*a*) 50 g. of iron-free stannous chloride dihydrate dissolved in 1 liter of 2*N* hydrochloric acid, (*b*) a saturated solution of mercuric chloride in water containing 5 ml. of 6*N* hydrochloric acid per liter, (*c*) 0.1*N* permanganate, and (*d*) approximately 0.1*N* ferric chloride, free from ferrous iron, in *N* hydrochloric acid. The directions below have been taken in part from those of Crowell, Luke, and Mastin.[92]

Adjust the sample to contain 0.15–0.25 g. of iron and 5 ml. of concentrated hydrochloric acid in a volume of about 25 ml. Heat to 90°C. and add stannous chloride solution until the yellow color disappears, then add 2 drops in excess and cool to 20–30°C. Pour in 10 ml. of mercuric chloride solution all at once, with thorough mixing. Let stand for at least 2, but not more than 5, minutes; then dilute with 400 ml. of water and introduce 25–50 ml. of Reinhardt-Zimmermann mixture (p. 78). Titrate with permanganate at a rate of about 1 ml. in 3 seconds, but more slowly near the end, to a faint pink color that persists for 15–30 seconds.

Run a blank with the same volumes of the reagents. First oxidize the stannous chloride with permanganate, then add 2 drops of stannous chloride in excess and continue as above. Just before titration add 25 ml. of the ferric chloride solution (or about as much as corresponds to the iron found) and allow the mixture to stand for 2 minutes or for the time that elapsed during titration of the sample. Titrate to the usual end-point.

Notes: (1) Meineke[93] demonstrated that mercurous chloride has some reducing action upon the ferric complex that is produced during titration. The action is the greater, the more calomel is present: hence the quantity of excess stannous chloride added initially should be closely limited. In every case the calomel should come down slowly as a silky or needle-like precipitate and not instantaneously in flocculent form. The latter is more easily oxidized and causes more difficulty with end-point recognition. Rapid addition of mercuric chloride, quick mixing, and presence of only a little stannous chloride are the required conditions. If much stannous ion is present some of the mercury may be reduced to metal, revealed by a grey to grey-black precipitate. It becomes impossible to titrate accurately when this happens.

(2) A few minutes must be allowed for the reaction between stannous chloride and mercuric chloride to reach completion.

(3) Crowell, Luke, and Mastin[92] found the stannous chloride method to give results about 0.08 per cent higher than the Jones reductor method under the best conditions.

(4) Elements that interfere[94] are vanadium, molybdenum, tungsten, platinum, and gold, all of which cause high results. The effect of tungsten is slight.

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[92] W. R. Crowell, W. W. Luke, and T. G. Mastin, *Ind. Eng. Chem., Anal. Ed.*, 13, 94 (1941); see also O. L. Barnebey, ref. 77.

[93] C. Meineke, *Z. öffentl. Chem.*, 4, 433 (1898).

[94] Cf. J. Knop, *J. Am. Chem. Soc.*, 46, 268 (1924); W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, Wiley, New York, 1929, pp. 301–302.

Amalgam Reduction (p. 18): Use of amalgamated zinc as a reducing agent for ferric iron is complicated by the fact that titanium, chromium, molybdenum, and vanadium are also reduced. Grimaldi, Stevens, and Carron[95] developed a procedure for iron in the presence of titanium and chromium in which the reoxidation of trivalent titanium by air is catalyzed by a trace of copper sulfate.[96]

The iron solution is made up to contain 10 ml. of concentrated sulfuric acid in 200 ml. and is passed through a Jones reductor at a rate of about 100 ml. per minute. To the reduced solution add 3 ml. of $0.0001M$ copper sulfate and bubble with air as vigorously as possible without the risk of losses by splashing. If the reduced solution was originally colorless, aerate for 5 minutes; if it becomes green, for 10 minutes. Otherwise, continue the aeration until 5 minutes after any violet color of titanous sulfate has disappeared. Prepare an indicator solution by adding $0.05N$ permanganate in fractional drops to 10 ml. of 10 per cent sulfuric acid containing 1-3 drops of ferrous *o*-phenanthroline (p. 127), until the red color just changes to blue. Into this mixture pour a small portion of the solution to be titrated and set it aside. Titrate the main portion with permanganate to the usual pink color (or to a grey-green if much chromium is present). Add the reserved mixture and continue titrating to the disappearance of the red indicator color. Determine and correct for the reagent blank.

In the absence of vanadium and molybdenum the method gives results within ±0.4 mg. of the true iron content, when from 30 to 250 mg. is taken. If chromium is quite low the titration can be done directly though somewhat less accurately, without phenanthroline.

Ishimaru[97] determines mixtures of iron and titanium by reducing both with a zinc amalgam and titrating the reduced solution with permanganate. He then reduces again and titrates the titanium(III) alone with standard ferric solution to a thiocyanate end-point. Presumably the reduced solutions are collected in an inert atmosphere to prevent oxidation by air.

Iron can be determined in the presence of titanium by passing the mixture through a silver reductor (p. 14). Only ferric iron is reduced and the ferrous solution can be titrated by any of the standard procedures.

(*d*) ***Metallic Iron:*** Riott[98] determines metallic iron in iron oxide mixtures by dissolving it in a mixture of potassium chloride, cupric chloride, and dilute acetic acid. Under the specified conditions, ferrous and ferric oxides are not attacked but metallic iron reacts:

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[95] F. S. Grimaldi, R. E. Stevens, and M. K. Carron, *Ind. Eng. Chem., Anal. Ed.*, **15**, 387 (1943); cf. W. M. McNabb and H. Skolnick, *ibid.*, **14**, 711 (1942); W. M. Thornton and R. Roseman, *J. Am. Chem. Soc.*, **57**, 619 (1935).

[96] E. Zintl and H. Wattenberg, *Ber.*, **56**, 477 (1923).

[97] S. Ishimaru, *J. Chem. Soc. Japan*, **59**, 667 (1938); *Chem. Abstr.*, **32**, 6171 (1938); cf., B. A. Shippy, *Anal. Chem.*, **21**, 698 (1949).

[98] J. P. Riott, *Ind. Eng. Chem., Anal. Ed.*, **13**, 546 (1941).

(*e*) ***Applications of the Ferrous-Permanganate Titration after Reduction of Ferric Salts:*** Very strong reducing agents such as stannous, titanous, and cuprous solutions give trouble when titrated with permanganate because the reactions are accompanied by appreciable air-oxidation. One can avoid this interference by adding an excess of ferric sulfate to form ferrous iron which can be titrated more accurately. Naturally, the titration can also be made with another standard oxidant such as ceric sulfate or potassium dichromate.

For the assay of *cuprous chloride,* Hatch and Estes[105] use a reagent consisting of 10 g. of ferric alum dissolved in enough $6N$ sulfuric acid to make 100 ml. A 0.3 g. sample of the cuprous chloride is weighed into a dry flask and treated with 25 ml. of the reagent. After the salt has been dissolved by swirling, 200 ml. of water and 5 ml. of phosphoric acid are added and the solution is titrated with $0.1N$ permanganate to a pink color which persists for 15 seconds. A correction for the reagent blank should be determined and subtracted.

In order to determine *cupric copper* one may reduce it, with glucose or arsenite in alkaline solution, to cuprous oxide. Köszegi[106] starts with a sample containing not more than 0.1–0.15 g. of copper in a volume of 50 ml. and reduces with 10 ml. of arsenite solution (4 g. of arsenious oxide and 3 g. of potassium carbonate heated with 100 ml. of water). Enough 10 per cent potassium hydroxide is added dropwise to dissolve the light green precipitate, then the solution is heated with stirring and kept at boiling for 5 minutes. The cuprous oxide is filtered on a sintered-glass or Gooch crucible and washed well with warm water. Köszegi dissolves the precipitate in a strongly acid ferric sulfate solution, but less induced air-oxidation occurs if a neutral ferric sulfate is used. After solution of the oxide, sulfuric acid is added and the ferrous iron is titrated with permanganate.

A reverse procedure can be applied for determination of *reducing sugars.* When the sugar sample is boiled with an excess of Fehling's solution, cuprous oxide is precipitated, although in somewhat empirical yield (see p. 357). The precipitate is collected, dissolved, and titrated as above.[107]

Hydroxylamine may be determined through its reducing properties.

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[105] L. F. Hatch and R. R. Estes, *Ind. Eng. Chem., Anal. Ed.*, **18**, 136 (1946).

[106] D. Köszegi, *Z. anal. Chem.*, **70**, 297 (1927).

[107] Cf. G. Bertrand, *Bull. soc. chim. France,* (3) **35**, 1285 (1906); N. Schoorl and A. Regenbogen, *Z. anal. Chem.*, **56**, 196 (1917).

In boiling acid solution the following reaction takes place with ferric iron:[108]

$$2NH_2OH + 4Fe^{3+} \rightarrow N_2O + 4Fe^{2+} + H_2O + 4H^+$$

Bray, Simpson, and Mackenzie[109] obtained good results by treating 25 ml. of about $0.1N$ hydroxylamine salt solution in an Erlenmeyer flask with 50 ml. of ferric sulfate reagent (40 g. of $Fe_2(SO_4)_3 \cdot 9H_2O$ per liter) and 15 ml. of 1:2 sulfuric acid, boiling for 5 minutes, cooling, diluting to about 100 ml., and titrating with permanganate. There is no interference from ammonium salts or small amounts of chloride.

For the determination of *bismuth*, Kubina and Plichta[110] treat a weakly acid solution, containing up to 0.25 g. of bismuth, with 0.1 g. of aluminum powder. After a 15 minute reaction period the mixture is cooled in a water bath while 40 ml. of 15 per cent potassium hydroxide is added, then warmed until the aluminum dissolves completely. The spongy precipitate of bismuth metal is filtered, washed, and dissolved in 15 ml. of a solution containing 200 g. ferric chloride and 250 ml. of hydrochloric acid per liter. Reinhardt-Zimmerman reagent is added and the solution is diluted greatly and titrated with $0.1N$ permanganate. It is important to make sure that all aluminum has reacted with the alkali; high results will otherwise be obtained. Probably the titration can be performed as well or better with dichromate and diphenylaminesulfonate (p. 177).

Ferrocyanide: The titration of potassium ferrocyanide with permanganate has already been described on p. 52.

$$Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + e$$

Following de Haen's development of the method, Kessler[111] obtained good results with determinations of ferrocyanide in hydrochloric acid solution. No side reaction between permanganate and chloride appears to be induced by the main reaction. As mentioned previously, best conditions for the titration are a suitable dilution (to

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[108] W. Meyeringh, *Ber.*, **10**, 1942 (1877); F. Raschig, *Ann.*, **241**, 188 (1887); *Z. angew. Chem.*, **17**, 1411 (1904); E. Ebler and E. Schott, *J. prakt. Chem.*, (2), **78**, 320 (1908); E. Rupp and H. Mäder, *Arch. Pharm.*, **251**, 297 (1913); F. Sommer and H. G. Templin, *Ber.*, **47**, 1227 (1914).

[109] W. C. Bray, M. E. Simpson, and A. A. Mackenzie, *J. Am. Chem. Soc.*, **41**, 1363 (1919).

[110] H. Kubina and J. Plichta, *Z. anal. Chem.*, **72**, 201 (1927). The use of magnesium for reduction of bismuth was studied by W. Strecker and A. Herrman, *ibid.*, **72**, 5 (1927) and by E. Rupp and G. Hamann, *ibid.*, **87**, 32 (1932).

[111] F. Kessler, *Ann. Phys. Chem.*, **119**, 241 (1863).

Molybdenum: In an inert atmosphere molybdenum is reduced to the trivalent state by various types of reductors (p. 17), with the exception of bismuth amalgam, silver, or mercury, which yield only the pentavalent form. Trivalent molybdenum is extremely sensitive to oxidation and should be reacted with a ferric solution without delay. Döring[124] studied the earlier procedure critically and gave the following directions.

The sample containing from 0.003 to 0.33 g. of molybdenum in 120 ml. of warm 6 per cent sulfuric acid is reduced slowly in a Jones reductor and is collected in an 800 ml. beaker with perforated cover glass, the beaker containing 35 ml. of a ferric solution per 0.1 g. of molybdenum. The ferric solution is prepared from 48.5 g. of ferric ammonium sulfate, 40 ml. of 85 per cent phosphoric acid, and 50 ml. of concentrated sulfuric acid per liter. While being stirred well, the brownish red mixture is titrated with $0.1N$ permanganate. Since zinc often contains a little iron, a blank should be run with the same volume of warm 6 per cent sulfuric acid in the reductor for the same length of time.

Notes: (1) It is generally more convenient to make use of a silver or mercury reductor and to titrate with ceric sulfate (p. 153).

(2) More recently zinc dust[125] or aluminum[126] has been recommended for the reduction.

(3) Cadmium may be determined[127] after precipitation as molybdate and filtration. The excess of molybdate in the filtrate is reduced with zinc amalgam and titrated with either permanganate or ceric sulfate.

Tungsten: Pfordten[128] appears to have been the first to reduce hexavalent tungsten to the tetravalent form with zinc and to titrate back with permanganate. He used 15 g. of stick zinc in warm 27 per cent hydrochloric acid solution and obtained reduction to a red-brown solution in 10 minutes. According to Someya,[129] zinc and cadmium amalgams are somewhat too reactive to be used conveniently. Someya preferred to carry out reduction in hydrochloric acid solution either with lead amalgam at 50°C., producing trivalent tungsten, or with bismuth amalgam, which yields tungsten(V). Since in either case permanganate titration produces tungsten(VI) again, various differential methods are possible. Treadwell and Nieriker[130] avoid the use of hydrochloric acid by reducing slowly in M phosphoric acid with a cadmium reductor; the solution is then better suited for titration with permanganate.

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[124] T. Döring, *Z. anal. Chem.*, **82**, 193 (1930); cf. D. L. Randall, *Am. J. Sci.*, (4) **24**, 313 (1907); G. G. Reissaus, *Metall u. Erz*, **21**, 118 (1924).

[125] E. Gagliardi and W. Pilz, *Monatsh.*, **82**, 1012 (1951).

[126] E. R. Riegel and R. D. Schwartz, *Anal. Chem.*, **26**, 410 (1954).

[127] V. K. Takagi, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*), **74**, 291 (1953).

[128] O. F. v. d. Pfordten, *Ann.*, **222**, 158 (1883); *Ber.*, **16**, 508 (1883); cf. E. Kuklin, *Stahl u. Eisen*, **24**, 27 (1904); O. Collenberg and J. Backer, *Z. Elektrochem.*, **30**, 230 (1924).

[129] K. Someya, *Z. anorg. u. allgem. Chem.*, **145**, 168 (1925).

Tungstate and Vanadate:[130] After reduction with cadmium, the products in M phosphoric acid are W(V) and V(II). The solution is caught under oxygen-free nitrogen and titrated with $0.1N$ permanganate, with exclusion of air (a ml.). A duplicate portion is reduced and is bubbled with nitrogen that contains several per cent of oxygen. Disappearance of the blue color indicates the formation of phosphotungstic acid, W(VI). Vanadium is now present in the green trivalent state and may be titrated with permanganate (b ml.). The quantity ($a - 1.5b$) represents the titration of W(V) to W(VI).

Tungstate and Iron:[130] Reduced as above, the mixture of W(V) and Fe(II) is titrated in the absence of oxygen. Another portion is partially oxidized by air after reduction and the iron alone is determined.

Uranium: In a Jones reductor uranium is reduced to the trivalent form, which is so unstable that at one time it was thought impossible to titrate reduced uranium accurately. Lundell and Knowles,[131] however, demonstrated that 5 minutes of shaking with air, at 20–25°C., raises all the uranium to tetravalence in a 1:20 sulfuric acid solution. The mixture can then be titrated with permanganate or with dichromate (p. 189). Tetravalent uranium is unstable in the presence of air at temperatures around 50°.

Someya,[132] working with oxygen-free solutions and a carbon dioxide atmosphere, obtained good results with zinc amalgam reduction in hydrochloric acid; under these conditions trivalent uranium is formed. With bismuth amalgam in 10–$12N$ sulfuric or 6–$12N$ hydrochloric acid, or lead amalgam in 5–$6N$ hydrochloric acid,[133] the uranium is obtained in the tetravalent state. Before titration the acid concentration (HCl) should be lowered to 2–$5N$ by dilution. The bismuth and zinc amalgam methods have been applied to determinations of phosphate after precipitation as uranyl ammonium phosphate.[134]

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[130] W. D. Treadwell and R. Nieriker, *Helv. Chim. Acta*, **24**, 1067, 1098 (1941).

[131] G. E. F. Lundell and H. B. Knowles, *J. Am. Chem. Soc.*, **47**, 2637 (1925); cf. G. Jander and K. Reeh, *Z. anorg. u. allgem. Chem.*, **129**, 293 (1923); T. Nakazono, *J. Chem. Soc. Japan*, **42**, 761 (1921).

[132] K. Someya, *Z. anorg. u. allgem. Chem.*, **152**, 376 (1926).

[133] K. Someya, *Z. anorg. u. allgem. Chem.*, **145**, 172 (1925).

[134] K. Someya, *Z. anorg. u. allgem. Chem.*, **152**, 382 (1926). See also G. Jander and K. Reeh, *ibid.*, **129**, 302 (1923).

Although other oxidizing titrants may be used (ferric sulfate, ceric sulfate, or potassium dichromate), permanganate is the only one which gives a satisfactory end-point at room temperature without the aid of a catalyst. Amalgamated zinc in a Jones reductor is the most convenient reductor, but with liquid zinc amalgams, provided that fresh amalgam is used each time, there is less interference from substances which are likely to plate out on the amalgam.[135]

Note: Since so many elements interfere in volumetric determinations of uranium, it is generally necessary to make preliminary separations. Cupferron precipitates iron, titanium, vanadium, and zirconium from cold, 3–4 N sulfuric acid, leaving hexavalent uranium in solution. Tetravalent uranium can be precipitated by the same reagent in cold, $2N$ sulfuric acid. After either step the cupferron is destroyed by fuming with nitric and sulfuric acids.[136] Nitrates must be expelled completely before reduction of the uranium is attempted.

Titanium: Air-free solutions of titanic salts are reduced at room temperature to the titanous state (trivalent) by zinc, zinc amalgam, or lead amalgam. Reduction can also be brought about with bismuth amalgam in hydrochloric acid solution at 60–70°C., or with a cadmium reductor (p. 155). The reduction product, protected from air, is titrated quantitatively back to tetravalence with permanganate.

Tschirch[137] determines titanium in organic mixtures by igniting, redissolving by fusion with sodium sulfate and concentrated sulfuric acid, diluting when cool, reducing in a Jones reductor, collecting in ferric sulfate solution, and titrating with permanganate.

If iron is also present in the sample, the reduction product should be titrated directly with ferric alum solution to a thiocyanate end-point (p. 647). Oxygen must be excluded.

In the analysis of nitrile, ilmenite, and other minerals, Colin[138] recommends the use of tannin to separate titanium from vanadium. The reduced solution is finally titrated with permanganate or dichromate.

Tin: Someya[139] described a permanganate titration method for tin after reduction from stannic to stannous with bismuth amalgam. The reduction takes place in $5–12N$ hydrochloric acid solution at

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[135] *Analytical Chemistry of Manhattan Project,* C. J. Rodden, ed., McGraw-Hill, 1950.

[136] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, Wiley, New York, 1929, pp. 110–111.

[137] E. Tschirch, *Pharm. Zentralhalle,* 75, 513 (1934).

[138] L. L. Colin, *J. Chem. Met. Mining Soc. S. Africa,* 50, 314 (1950).

[139] K. Someya, *Z. anorg. u. allgem. Chem.,* 160, 404 (1927).

45°C., during a shaking period of at least 10 minutes. An inert atmosphere is required. Cupric sulfate is reduced to cuprous under the same conditions. For most purposes the iodometric determination of tin is to be preferred.

Chromium: Applicability of the Jones reductor to determinations of chromium was pointed out by van Brunt,[140] who designed an electrically heated apparatus to facilitate reduction of titanium or chromium. Divalent chromium is such an active reducing agent that it liberates hydrogen from hydrochloric acid solutions stronger than about $2.5N$. Preferably the solution should be caught in an excess of ferric alum so that one titrates ferrous ion instead of chromous.

Someya[141] obtained quantitative reduction of chromic solutions to chromous with zinc or lead amalgams in hydrochloric acid. Sulfuric acid interferes with reduction but moderate amounts of phosphoric acid do not. An inert atmosphere is essential; Someya used carbon dioxide. The titration could be made with permanganate or with dichromate and diphenylamine, as well as with iodine, iodate, or bromate.

Columbium: The optimum conditions for the reduction of columbium(V) to columbium(III) by means of zinc amalgam with subsequent titration back to the pentavalent state with permanganate were studied by Knowles and Lundell,[142] for only one earlier investigator[143] was able to obtain stoichiometric results. They observed that special attention must be given to the preparation of the zinc amalgam, to the length of the column, the acidity, the temperature, and the concentration of columbium for satisfactory results to be obtained.

Preparation of the Zinc Amalgam: Place 1000 g. of 20 mesh zinc (low in iron content) in a stout, wide-mouthed glass bottle, add 500 ml. of a 2 per cent solution of mercuric chloride, mix for 45–60 seconds, discard the solution, and wash 5 times with distilled water. Add 500 ml. of warm sulfuric acid (1 :99) to the washed amalgam, mix, discard the solution, and wash well with distilled water. Store the amalgam under water to which a few drops of hydrochloric acid have been added.

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[140] C. van Brunt, *J. Am. Chem. Soc.*, **36**, 1426 (1914).

[141] K. Someya, *Z. anorg. u. allgem. Chem.*, **160**, 355 (1927); **169**, 297 (1928); for an application to chromium in steel see Someya, *ibid.*, **175**, 352 (1928).

[142] H. B. Knowles and G. E. F. Lundell, *J. Research Natl. Bur. Standards*, **42** 405 (1949).

[143] T. R. Cunningham, *Ind. Eng. Chem., Anal. Ed.*, **10**, 233 (1938).

Procedure: Fuse the dried sample (not more than 300 mg. of Cb_2O_5) in a 25 ml. covered silica crucible with 3–5 g. of potassium pyrosulfate. Cool, transfer the crucible and cover to a covered 250 ml. beaker, add 20 ml. of sulfuric acid, and heat moderately to dissolve the mass. Cool, add 1–2 ml. of 30 per cent hydrogen peroxide, dilute cautiously with 100 ml. of water, and rinse and remove the crucible and its cover. Cool, add 20 ml. of sulfuric acid, dilute to 200 ml. with water, add 2 g. of succinic acid, and heat while stirring until the succinic acid dissolves. Pretreat the column (33 × 1 inch) as follows: wash with hot dilute sulfuric acid (1:19) followed by hot water and discard the washings. Place a three-fold excess of ferric iron in the receiver and attach the latter to the reductor. Pass 100 ml. of sulfuric acid (1:4) heated to 65° ± 5°C. through the reductor. Draw this solution into the receiver with the aid of suction and then follow with the test solution, 150 ml. of sulfuric acid (1:4) containing 1 per cent of succinic acid (each solution being at a temperature of 65° ± 5°C.), and finally 200–250 ml. of cold water, slowly and without interruption at a constant rate so that the total time of passage for all solutions is not less than 25 minutes. Owing to gas evolution, the column alternately fills and empties, but this effect can be ignored. Cool the receiver in ice water during the reduction process. Remove the receiver and drain the outlet tube in the usual way, add 10 ml. of 85 per cent phosphoric acid, and titrate with 0.1*N* permanganate solution, using *o*-phenanthroline as indicator.

Run a blank on all reagents by following the above procedure exactly. To ensure the absence of oxidizable impurities all the acid-wash solutions are treated while hot with a few drops of permanganate solution.

Notes: (1) The zinc must be coated only lightly with mercury; hence its useful life is limited.

(2) The optimum acidity is 15–20 per cent of sulfuric acid. At the lower concentration slightly low but acceptable results are obtained. At acidities lower than 15 per cent the reduced solution is dark-colored instead of amethyst and gives low results. At an acidity of 20 per cent slightly high results are obtained owing to the formation of traces of hydrogen sulfide.

(3) Succinic acid is introduced to prevent hydrolysis; it has no harmful effect on the reduction process.

(4) The concentration of columbium should not exceed 1 mg. per milliliter in the 33 × 1 inch reductor. When the amount of Cb_2O_5 is not more than 175 mg., a shorter column (18 × 1 inch) may be used, but the concentration should not exceed 0.7–0.8 mg. per milliliter.

(5) The heating of the solutions is not essential, but it facilitates the diffusion of zinc through the amalgam and produces a more vigorous action.

(6) Although it has been claimed that titanium must be present to ensure complete reduction,[144] this does not appear to be necessary.

Rhenium: Lundell and Knowles[145] determine rhenium by reducing to rhenium hydride in a Jones reductor and titrating back to perrhenate with permanganate. The valence change is from −1 to +7.

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[144] W. D. Treadwell, *Helv. Chim. Acta*, 5, 806 (1922).

[145] G. E. F. Lundell and H. B. Knowles, *J. Research Natl. Bur. Standards*, 18, 629 (1937). See also O. Tomíček and F. Tomíček, *Collection Czech Chem. Communs.*, 11, 626 (1939).

Procedure: The sample is prepared so that not more than 15 mg. of rhenium is present in 500 ml. of solution containing 12.5 ml. of concentrated sulfuric acid. This solution and 150 ml. of 1:19 sulfuric acid are boiled separately, while carbon dioxide is passed through to expel oxygen, and are cooled to 5°C. under a carbon dioxide atmosphere. An excess of ferric sulfate solution is placed in the receiving flask of the reductor. First 50 ml. of the cooled acid is passed through amalgamated zinc in the reductor, followed by the sample solution and then by the remaining acid. Ferrous iron formed in the receiver is titrated with $0.05N$ permanganate.

Notes: (1) Because of the heat of reaction one should not attempt to reduce a solution that is richer in rhenium or has a higher acid concentration. Tomíček and Tomíček[145] recommended the use of a modified reductor cooled with ice.

(2) The reduced solution may also be caught in an excess of permanganate which is then treated with standard ferrous solution and adjusted to a permanganate end-point. In either case, a blank should be carried through the same procedure.

Volhard Method for Manganese. If a manganous salt solution is warmed with permanganate, it turns brown and a dark precipitate soon appears. Manganous ion is oxidized and permanganate reduced, both going to hydrous manganese dioxide. Guyard[146] utilized the reaction for determining manganese and Volhard[147] improved the procedure.

During titration of a neutral solution, permanganate is consumed in accordance with the equation

$$3\text{Mn}^{2+} + 2\text{MnO}_4^- + 2\text{H}_2\text{O} \longrightarrow 5\text{MnO}_2 + 4\text{H}^+$$

but the result is usually somewhat low. Hydrated manganese dioxide has acid properties and adsorbs manganous hydroxide, preventing complete oxidation. The difficulty can be avoided, as Volhard demonstrated, by introducing a sufficient amount of calcium, magnesium, barium, or zinc salt. These cations are adsorbed preferentially,[148] leaving manganous ions in the solution free to react. Much literature has accumulated concerning the titration,[149] but we shall mention only the more important findings.

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[146] A. Guyard, *Bull. soc. chim. France*, **6**, 89 (1864).

[147] J. Volhard, *Ann.*, **198**, 318 (1879).

[148] Cf. P. B. Sarkar and N. R. Dhar, *Z. anorg. u. allgem. Chem.*, **121**, 135 (1922).

[149] C. Meineke, *Z. anal. Chem.*, **24**, 423 (1885); E. Hintz, *ibid.*, **24**, 421 (1885); N. Wolff, *Stahl. u. Eisen*, **4**, 702 (1884); **11**, 377 (1891); H. Weber, *Z. anal. Chem.*, **43**, 564, 643 (1904); E. Deiss, *Chem. Ztg.*, **34**, 237 (1910); H. Beckurts, *Die Methoden der Massanalyse*, Vieweg, Braunschweig, 1913, p. 562.

Whereas Volhard proceeded by titrating only a weak nitric acid solution, at boiling, Wolff[149] recommended a small addition of zinc oxide. Finding that the errors were not completely eliminated thereby, Meineke[149] treated with 25–30 g. of zinc sulfate, introduced an excess of permanganate, and titrated the excess after filtration through asbestos. The indirect titration has also been employed by others, bur a direct method is preferable. Fischer[150] obtained results about 4 per cent low according to Volhard's directions; as causes he listed adsorption of manganous ions by the oxide and partial precipitation of manganese as manganite. Fischer brought about considerable improvement by titrating to an apparent end-point in neutral solution, then acidifying with acetic acid and completing the titration.

Procedure of Fischer: To 500 ml. of the very faintly acid sample solution add 1.0–1.5 g. of zinc oxide plus 10–20 g. of zinc sulfate. Heat to boiling and, while swirling, titrate with just enough permanganate to produce a pink color in the solution when the precipitate is allowed to settle. Then acidify with 1 ml. of acetic acid and complete the titration to a permanent pink. Run a blank on a mixture of the reagents in the same total volume.

Kolthoff[151] obtained good results by Fischer's method but found that only 1 g. of zinc sulfate is necessary. Furthermore, with the use of pure zinc oxide in neutral solution the reaction proceeds practically quantitatively in accordance with the equation on p. 97. Barely a trace of additional permanganate is required after acidification. Neither is it essential that zinc oxide be present, for the determination can be carried out on a solution buffered with acetic acid and sodium acetate (formate-free) and containing zinc sulfate. In such a medium manganese dioxide does not precipitate as rapidly at the beginning. Shortly before the equivalence point the supernatant liquid is still quite brown. With further addition of permanganate, boiling, and vigorous shaking, the suspension flocculates rapidly just before the end-point. Larger quantities of sodium acetate (5 g. to 400 ml.) cause the system to behave the same as in titration of a neutral solution.

Reinitzer and Conrath[152] independently studied the titration of acetate-buffered solutions and noted that the precipitate settles well in great flocs without sticking to the sides of the beaker. For a titration with 10 ml. of

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[150] W. M. Fischer, *Z. anal. Chem.*, 48, 751 (1909).

[151] I. M. Kolthoff, *Pharm. Weekblad*, 61, 1141 (1924).

[152] B. Reinitzer and P. Conrath, *Z. anal. Chem.*, 68, 129 (1926).

0.1N permanganate they used 2 g. of sodium acetate per 300–400 ml. of solution. Among other advantages of the acetate system they mentioned that in it the manganese dioxide is formed rapidly and is free from lower oxides of manganese. If ferric iron is also present, it precipitates as a basic acetate and does not interfere with the end-point.

Some preparations of sodium acetate contain formate, which interferes by consuming permanganate. Reinitzer and Conrath[153] gave the following methods for detecting and eliminating reducing impurities.

Add 3 drops of 0.1N permanganate to 300 ml. of boiling distilled water. If the water is pure, as indicated by its remaining light pink for at least 5 minutes, put in 5 g. of sodium acetate. The solution should remain clear and perceptibly pink after 5 minutes of boiling. To purify the salt, dissolve 30–40 g. in 500 ml. of boiling water and add 0.1N permanganate gradually until the rate of decoloration becomes very slow. This may require several hours. Finally remove suspended manganese oxides on a glass or porcelain filter and evaporate the clear filtrate to dryness on a steam bath. The solution cannot be kept for long as such, because fungus growth produces new impurities.

Kolthoff regards the modified Fischer method as more satisfactory for manganese determination than Reinitzer and Conrath's procedure. This is confirmed by the work of Wohlmann,[154] who failed to obtain theoretical results with the latter. The use of some zinc sulfate (1–5 g.) is unconditionally necessary. The excess of zinc oxide added should be small, since otherwise the precipitate does not settle readily and recognition of the end-point is difficult.

For micro work, Mika[155] specified the following conditions: Prepare the sample to contain 0.8–1.0 mg. of manganese in 5 ml. of neutral solution in a graduate. Add 1 g. of zinc acetate (which has been tested for purity—see method above—as for sodium acetate) and 0.5 ml. of 2N acetic acid. Titrate with 0.01N permanganate dropwise with thorough stirring and add a small excess. Observe the volume, allow the precipitate to settle, and take a generous aliquot portion of the clear solution for back-titration. Add 2 ml. of 4N sulfuric acid followed by a crystal of potassium iodide and titrate the liberated iodine with 0.01N thiosulfate.

Other Permanganate Methods for Manganese: Hillson[156] described a procedure in which manganese is oxidized to permanganate in a phosphate-phosphoric acid solution with persulfate; the excess of the latter is decomposed by boiling, and the permanganate is titrated with standard arsenite. Details are given on p. 658 along with other arsenite methods. However, the oxidized sample and a blank can also be treated with equal volumes of unstandardized arsenite and titrated back with standard permanganate

[153] B. Reinitzer and P. Conrath, *Z. anal. Chem.*, 68, 81 (1926).

[154] E. Wohlmann, *Z. anal. Chem.*, 89, 321 (1932).

[155] J. Mika, *Z. anal. Chem.*, 78, 268 (1929).

[156] H. D. Hillson, *Ind. Eng. Chem., Anal. Ed.*, 16, 560 (1944).

Osmium tetroxide must be used as catalyst for the arsenite-permanganate reaction.

According to Zvenigorodskaya,[157] if sufficient fluoride is present it is possible to titrate manganese to the trivalent state with permanganate:

$$4Mn^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Mn^{3+} + 4H_2O$$

The sample, containing not more than 30 mg. of manganese in divalent condition, is treated with 2–3 g. of ammonium chloride and neutralized with ammonia. Add 15 ml. of 4*N* hydrochloric acid, cool to less than 10 °C., add 6 g. of ammonium fluoride, and titrate with 0.1*N* permanganate while stirring thoroughly. The end-point is a change from a light pinkish brown to a definite, persistent pink after addition of 1–2 drops of permanganate in excess (blank correction). The presence of calcium and magnesium salts or silica is unfavorable.

A somewhat similar procedure employing dihydrogen pyrophosphate as the complexing agent has been described by Lingane and Karplus,[158] but because of the color of manganese(III) pyrophosphate complex they found it necessary to titrate potentiometrically.

Issa and Hewaidy[159] have described a method in which manganese(II) is oxidized to manganese(IV) with alkaline hydrogen peroxide and stabilized by tellurate,[160] which also ensures smooth and quantitative oxidation to the quadrivalent state.

Procedure: The solution should be 0.1*N* in sulfuric acid and should contain 3–55 mg. of manganese. Add 0.08 g. of telluric acid for every 5 mg. of manganese present and stir until dissolution is complete. Neutralize with 5*N* sodium hydroxide solution and add sufficient in excess to give a final concentration of 2.5*N*. Add about 0.2 ml. of 20 vol. hydrogen peroxide for each 5 mg. of manganese and stir or shake until the solution becomes clear or reddish in color. Heat to about 60°C. for about 10 minutes and then just bring to the boiling point to destroy the excess of hydrogen peroxide.

Add a measured excess of 0.1*N* oxalic acid solution to the hot solution and then an excess of 2*M* sulfuric acid. Titrate the excess of oxalic acid at 60–80°C. with 0.1*N* permanganate solution.

Alternatively, cool the solution, add an excess of 0.1*N* ferrous ammonium sulfate solution, and titrate back with permanganate.

Notes: (1) In the absence of telluric acid, manganese dioxide and some lower oxides are formed and the results are low.

(2) Telluric acid can be added in amounts up to 0.15 g. per 5 mg. of manganese

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[157] V. M. Zvenigorodskaya, *Zavodskaya Lab.*, **12**, 152 (1947); *Chem. Abstr.*, **41**, 5662 (1946).

[158] J. J. Lingane and R. Karplus, *Ind. Eng. Chem., Anal. Ed.*, **18**, 191 (1946).

[159] I. M. Issa and I. F. Hewaidy, *Chemist Analyst*, **44**, 70 (1955).

[160] O. Tomíček, O. Pročke, and V. Pavelka, *Collection Czech Chem. Communs.*, **11**, 449 (1939).

without affecting the results. If the stated amount of hydrogen peroxide is exceeded, low results are obtained.

(3) If the hot solution is acidified before the addition of oxalic acid, or the ferrous solution is added to the cold solution before acidification, considerable errors occur. These are due respectively to the decomposition of manganese(IV) in hot acid solution and to atmospheric oxidation of ferrous ion in an alkaline solution.

Chromium: Permanganate oxidizes chromic ions in acid solution or, better still, in neutral or alkaline medium to chromic acid or chromate.

Donath[161] let the neutral chromic salt solution flow into boiling permanganate made strongly alkaline with sodium carbonate and sodium hydroxide, until the liquid showing above the rapid-settling precipitate became a clear yellow with no trace of redness. According to Bollenbach,[162] the trivalent chromium salt should be greatly diluted with weak nitric acid and should be treated with much potassium nitrate, barium sulfate, and lead nitrate. Titration of the boiling mixture with permanganate produces lead chromate (difficultly soluble in very dilute acid) and the end-point is shown by a change toward pink.

Reinitzer and Conrath[163] found the slow course of the reaction to be a serious disadvantage; this is apparently caused by too high a concentration of mineral acid. If sodium acetate is added, the reaction becomes

$$Cr^{3+} + MnO_4^- + 4OH^- \longrightarrow CrO_4^{2-} + MnO_2 + 2H_2O$$

Acetate hinders not only the precipitation of basic chromic salts but also the formation of chromic chromate. For the most rapid reaction rate it is necessary to add a disproportionately great excess of sodium acetate and to work at high dilution of the chromium.

Procedure:[163] A sample containing 10–15 mg. of chromium in the trivalent condition is placed in a flask, diluted to 300–400 ml., and treated with about 2 g. of sodium acetate. The clear solution is heated to boiling and titrated at the boiling point with 0.1*N* permanganate. With continued vigorous shaking, the manganese dioxide that is produced will separate in quick-settling form. The first drops of permanganate in excess bring about a change from pure chromate yellow to orange-yellow. It is advantageous to have some barium salt present, for then barium chromate precipitates and the end-point can be recognized more easily.

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[161] E. Donath, *Ber.*, **14**, 982 (1881).

[162] H. Bollenbach, *Chem. Ztg.*, **31**, 760 (1907).

[163] B. Reinitzer and P. Conrath, *Z. anal. Chem.*, **68**, 81 (1926).

Notes: (1) The sodium acetate used should be tested for purity as described on p. 99. The amount taken may vary within wide limits, 2–3 g. being sufficient for a 10 ml. titration.

(2) Titration of a more concentrated chromic solution is not recommended; toward the end the reaction proceeds more and more slowly, so that low results are probable. A volume of 500 ml. for 10 ml. of 0.1N permanganate consumed is satisfactory.

(3) Small quantities of iron do not interfere. Reinitzer and Conrath[163] developed a barium carbonate separation method for use with larger amounts.

(4) The oxidation of chromic salts with permanganate in sulfuric acid solution is an autocatalytic process. The intermediate formation of tri- and tetravalent manganese ions strongly favors oxidation, according to Fales and Roller.[164] The reaction mechanism thus resembles that for the oxidation of oxalic acid.

Thallium: Willm[165] early studied the permanganate titration of thallous solutions and noted that heat and the presence of chloride ions are required. Various other workers confirmed these findings but obtained high results, particularly when small quantities were present. Jilek and Lukas[166] sought to improve the procedure by making certain through sulfur dioxide reduction that all thallium is present in the monovalent state, and by adding potassium chloride to the solution before titration. Swift and Garner[167] obtained results about 0.4 per cent high by the Jilek-Lukas method; apparently some free chlorine or hypochlorite is formed. They were unable to improve the method by adding phosphoric acid or manganous sulfate, or by titrating to an iodine monochloride end-point. Beale, Hutchison, and Chandlee,[168] however, found that good results are possible if sufficient fluoride is present. Under these conditions the permanganate is reduced to trivalent manganese and its normality is only four fifths of that ordinarily determined. They proposed the following method.

Procedure: Prepare the sample so that from 6 to 100 mg. of monovalent thallium, free from interfering elements, is present in 60 ml. of 1:10 hydrochloric acid. Add 3.0 g. of powdered sodium fluoride or a filtered solution containing 7.0 g. of potassium fluoride dihydrate. Titrate with 0.005M (0.02N) permanganate at room temperature to a faint pink color which should persist for several minutes. A slight brown color may appear as the titration progresses, but the end-point is easily recognized. One milliliter of 0.005M permanganate is equivalent to 2.044 mg. of thallium.

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[164] H. A. Fales and P. S. Roller, *J. Am. Chem. Soc.*, **51**, 345 (1929).

[165] E. Willm, *Bull. soc. chim. France*, **5**, 352 (1863).

[166] A. Jilek and J. Lukas, *Collection Czech Chem. Communs.*, **1**, 83 (1929). For earlier literature see this paper and the following two references.

[167] E. H. Swift and C. S. Garner, *J. Am. Chem. Soc.*, **58**, 113 (1936).

[168] R. S. Beale, A. W. Hutchison, and G. C. Chandlee, *Ind. Eng. Chem., Anal. Ed.*, **13**, 240 (1941).

Note: Various elements interfere in the method. An effective method of separating thallium from a number of substances is one proposed by Wada and Ishii,[169] who extract thallic bromide from *N* hydrobromic acid solution with ether. After evaporation of the ether, the thallium bromide may be converted to chloride by successive double evaporations, first with nitric acid and finally with hydrochloric. The trivalent thallium is reduced to thallium(I) by treatment with sulfur dioxide and the excess of the latter is expelled by boiling in dilute hydrochloric acid solution. Since thallous halides are not very soluble, sufficient dilution should be allowed during and after reduction.

Platinum: According to Grünberg and Golbrich,[170] tetravalent platinum in the form of chloroplatinic acid can be reduced to the divalent state with an excess of cuprous chloride. The excess is oxidized by passing air through for 4 hours, then sulfuric acid and manganous sulfate are added and the solution is titrated with permanganate. The color change is from pale yellow to orange.

2. Methods for Organic Substances. Few organic compounds can be determined by direct titration with permanganate. Although under suitable conditions some of them can be decomposed completely to carbon dioxide and water, the reactions are usually slow so that one must work with an excess of permanganate and titrate it back at the end. Such methods will be considered later (p. 113), but first we shall discuss the materials which can be titrated directly.

Oxalic Acid: The reaction between permanganate and oxalic acid has been discussed on pp. 48–52, where the sources of error in the determination are also listed. At about 60°C. the oxidation proceeds according to the equation

$$H_2C_2O_4 + O \longrightarrow H_2O + 2CO_2$$

After the first few drops of permanganate have been decolored, one can titrate directly to the end-point. In principle it is better to add somewhat less than the required amount of permanganate to an oxalate-sulfuric acid solution before heating and then complete the titration at 55–60° C. (procedure of Fowler and Bright). However, one must know fairly closely the quantity of oxalate present in the sample in order to follow this course.

If the acidity is too low, a precipitate of manganese dioxide will be formed during titration.

Contradictory data have been published regarding the effect of chloride ions. The investigations of Zimmermann,[171] Wagner,[172] and others indicated that the titration could be done as well in hydrochloric acid solution as in sulfuric acid. Gooch and Peters,[173] on the other hand, demonstrated that a reaction between chloride and permanganate is induced during oxidation of oxalic acid, but that addition of a manganous salt eliminates the error. Baxter and Zanetti[174] encountered no irregularity in titrating when the initial temperature of the hydrochloric acid-oxalic acid solution exceeded 70°C.; below this temperature more than the theoretical amount of permanganate was consumed and the solution smelled of hypochlorous acid. Kolthoff[175] confirmed these findings and noted also that at the same temperature and acidity the temporarily persisting first color of permanganate fades more rapidly in hydrochloric acid solution than in sulfuric acid.

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[169] I. Wada and R. Ishii, *Sci. Papers Inst. Phys. Chem. Research Tokyo*, **24**, 135 (1934); *Chem. Abstr.*, **28**, 3334, 5364 (1934).

[170] A. A. Grünberg and Z. E. Golbrich, *J. Gen. Chem. U.S.S.R.*, **14**, 808 (1944); *Brit. Abstr.*, **1946**, C81.

Many metal ions are practically without effect on the reaction. Only in the presence of much magnesium salt at boiling does there seem to be a slight overconsumption of permanganate. The foregoing observations may be summarized by saying that above an initial temperature of 70°C. the titration gives good results in hydrochloric acid solution and no addition of manganous salt is necessary.

According to Ehrenfeld[176] oxalic acid in neutral solution is only partly oxidized by permanganate at 100°C. The method gives erratic results and has no practical importance. Oxalate is not oxidized by permanganate in alkaline medium.

Determination of Metals as Oxalates: Any metal which is precipitated quantitatively as an oxalate may be determined by titration with permanganate.[177] Since numerous elements fall into this category, the method is not at all specific for any one; it is therefore necessary that interfering metals be absent. If this condition is met, the method can be used for determination of calcium, strontium, magnesium, nickel, cobalt, cadmium, zinc, copper, lead, mercury, silver, bismuth, cerium, and the rare earth elements.

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[171] C. Zimmermann, *Ann.*, **213**, 312 (1882).

[172] J. Wagner, *Z. physik. Chem.*, **28**, 35 (1899).

[173] F. A. Gooch and C. A. Peters, *Z. anorg. Chem.*, **21**, 185 (1899); *Am. J. Sci.*, **7**, 461 (1899).

[174] G. P. Baxter and J. E. Zanetti, *Am. Chem. J.*, **33**, 500 (1905).

[175] I. M. Kolthoff, *Z. anal. Chem.*, **64**, 204 (1924).

[176] R. Ehrenfeld, *Z. anorg. Chem.*, **33**, 118 (1903).

[177] Cf. C. Luckow, *Z. anal. Chem.*, **26**, 9 (1887); H. Beckurts, *Die Methoden der Massanalyse,* Vieweg, Braunschweig, 1913, pp. 614–619.

Calcium: The volumetric determination of calcium has considerable significance and will be discussed in some detail. In the usual case, most interfering elements are removed by preliminary precipitations with hydrogen sulfide, ammonium hydroxide, or both. Calcium and strontium are then determined together after oxalate precipitation under conditions which leave magnesium in solution. The determination may be carried out in either of two ways:

(1) One precipitates with a measured excess of oxalate, dilutes to a definite volume with water, and titrates an aliquot portion after filtering or allowing to settle.

(2) One precipitates with excess oxalate and filters quantitatively, bearing in mind the appreciable water-solubility of calcium oxalate. In dilute alcohol the solubility is very small but, if alcohol is employed, it is necessary to dry the precipitate after filtering to prevent interference with the titration. The precipitate is dissolved in sulfuric or hydrochloric acid (preferably the latter, so far as the solubility of the calcium salt is concerned) and the solution is titrated at 80°C. Simpson[178] believed that the use of filter paper leads to an error through a side reaction with permanganate (cf. p. 38). Kolthoff confirmed that in acid solution filter paper consumes permanganate, more with greater concentrations and with longer times of contact. During an oxalate titration there is a significant quantity of permanganate present only during the incubation period, so the error can be diminished by adding manganous salt and by keeping the paper out of the mixture until the incubation period is over. Nevertheless, it is preferable to filter on asbestos or on a porous-bottom crucible.

Procedure:[179] Weigh out a sample containing 0.07–0.09 g. of calcium, neutralize to methyl red, add 5 ml. of concentrated hydrochloric acid, and bring to a volume of about 200 ml. Introduce 50 ml. of a solution containing 3 g. of ammonium oxalate monohydrate (1 g. will serve if calcium is the only cation, but 5–6 g. should be taken if 0.1 g. of magnesium is present). Warm to 70–80°C. Neutralize with 1:1 ammonium hydroxide, allow to stand for 1 hour, and filter on a sintered-glass or porous porcelain filter or a Gooch crucible. If necessary (Note 1), dissolve in warm 1:4 hydrochloric acid and reprecipitate. Wash with cold water until free from chloride, but avoid using an excess. Take care to wash soluble oxalate from the sides and bottom of the crucible. Dissolve the precipitate by adding small portions of warm 1:8 sulfuric acid, allowing 1 or 2 minutes and stirring with a short glass rod each time before drawing the solution through into a clean receiver. Dilute to an acidity of 1–1.5N, heat to 80°C., and titrate to the first moderately persistent pink. Correct for a blank on the reagents, taken to the same end-point.

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[178] S. G. Simpson, *Ind. Eng. Chem.*, **13**, 1152 (1921).

[179] I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, 2nd ed., Macmillan, New York, 1943, p. 606; cf. A. Lassieur, *Chim. anal.*, **29**, 197 (1947).

Notes: (1) If sodium is present, a small but significant quantity is likely to be coprecipitated with the calcium.[180] Potassium is not carried down appreciably. Reprecipitation is advisable if the original solution contains as much magnesium as calcium. The interference of manganese or barium is practically negligible if two precipitations are made.

(2) The procedure given above is not applicable to samples having high ratios of magnesium to calcium. Up to 0.5 g. of magnesium can be held in 100 ml. of solution at 80° C. if sufficient ammonium oxalate is present, the latter forming a soluble complex with magnesium,[181] but the solubility of calcium oxalate is increased in this medium. A correction of 2.0 mg. of calcium per 100 ml. may be applied under these conditions.

(3) Larger amounts of magnesium may be removed by treatment with 95–98 per cent of the theoretical quantity of sodium hydroxide. The precipitation is made in a known volume and an aliquot portion of the clear liquid is taken after settling.[182] Calcium remains in solution and may be determined by double oxalate precipitation. It is not necessary to have sugar or mannitol present during the formation of magnesium hydroxide, as is sometimes specified. A blank should be run on the caustic soda, which is likely to contain a trace of strontium.

(4) Garwin and Hixson[183] found that in solutions containing sufficient ammonia to convert nickel and cobalt to ammines, calcium is completely precipitated with a slight excess of 4 per cent ammonium oxalate solution. Nickel is determined in the filtrate with dimethylglyoxime.

Magnesium. In water, magnesium oxalate is too soluble to precipitate quantitatively and its rate of formation is slow. Addition of much acetic acid lowers the solubility and increases the rate.[184] Elving and Caley[185] obtained quantitative precipitation and accurate results when the final concentration of acetic acid was 85 per cent by volume and the precipitate was washed with 85 per cent acetic acid.

[180] I. M. Kolthoff and E. B. Sandell, *J. Phys. Chem.*, **37**, 443 (1933).

[181] E. R. Wright and R. H. Delaune, *Ind. Eng. Chem., Anal. Ed.*, **18**, 426 (1946); M. Bobtelsky and Frau Malkowa-Janowski, *Z. angew. Chem.*, **40**, 1434 (1927); Z. Karaoglanov, *Z. anal. Chem.*, **124**, 102 (1942).

[182] C. F. Prutton, unpublished experiments, August, 1925; W. M. Hazel and W. K. Eglof, *Ind. Eng. Chem., Anal. Ed.*, **18**, 759 (1946); J. A. Greear and E. R. Wright, *Anal. Chem.*, **21**, 596 (1949).

[183] L. Garwin and A. N. Hixson, *Anal. Chem.*, **21**, 1215 (1949).

[184] A. Souchay and E. Lenssen, *Ann.*, **99**, 31 (1856); A. Classen, *Z. anal. Chem.*, **18**, 373 (1879); G. Nass, *Z. angew. Chem.*, **7**, 501 (1894).

[185] P. J. Elving and E. R. Caley, *Ind. Eng. Chem., Anal. Ed.*, **9**, 558 (1937).

For volumetric analysis they precipitated in a centrifuge tube, since it was found difficult to remove all excess oxalate from a filter paper with the specified wash solution. The precipitate and mother liquor were digested together on a steam bath for an hour before centrifuging. After three or more washings, the precipitate was dissolved in 5 per cent sulfuric acid and titrated with permanganate.

Because the magnesium oxalate formed in ordinary precipitation is finely divided and difficult to filter, Gordon and Caley[186] precipitate magnesium from 85 per cent acetic acid medium by slowly hydrolyzing dissolved ethyl oxalate. In order to keep the pH high enough, ammonium acetate is added as a buffer. With slow hydrolysis the oxalate-ion concentration remains small and large crystals of magnesium oxalate are formed. Good results can be obtained with as little as 10 mg. of magnesium.

Procedure: Since calcium and other interfering elements must be absent, it is convenient to work with the oxalate filtrate from a calcium determination. Ammonium salts are removed by evaporation with nitric acid, and oxalate is destroyed with a mixture of nitric and perchloric acids. The perchlorate residue is dissolved, neutralized if necessary, and brought to a volume of 14–15 ml. Not more than 50–55 mg. of magnesium should be present. Add 75 ml. of glacial acetic acid, mix well, and follow with 10 ml. of acetic acid containing 1 g. of ammonium acetate. Finally introduce 1.5 ml. of ethyl oxalate and stir thoroughly. Cover the beaker with a watch glass, heat to approximately 100°C., and keep at this temperature for 2 hours after precipitation begins. Then add 5 ml. of 85 per cent acetic acid saturated with ammonium oxalate at room temperature and keep hot 15 minutes longer.

While hot, filter on a glass or porcelain filter crucible of medium porosity. Transfer the precipitate to the crucible with the aid of a rubber-tipped stirring rod and several portions of warm 85 per cent acetic acid. After washing sufficiently, dissolve the magnesium oxalate into a clean flask with a total of 200 ml. of 5 per cent sulfuric acid at 80°C. Titrate at once with standard $0.1N$ permanganate. One milliliter is equivalent to 1.216 mg. of magnesium.

Sulfate interferes, but chloride and perchlorate do not. Moderate amounts of alkali metals (100 mg. or less) are not objectionable.

Zinc: In a 70 per cent solution of acetic acid, zinc can be completely precipitated as the oxalate. Elving and Lamkin[187] have described a direct precipitation procedure similar to that originally used for magnesium[185] and have applied it to the determination of zinc in brasses and bronzes.

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[186] L. Gordon and E. R. Caley, *Anal. Chem.*, 20, 560 (1948).

[187] P. J. Elving and J. C. Lamkin, *Ind. Eng. Chem., Anal. Ed.*, 16, 194 (1944).

Matsumoto[188] precipitates at a pH of 3.1–4.4 by adding dilute ammonia solution to the slightly acid solution containing oxalic acid. The precipitate is washed with 50 per cent ethanol or methanol after standing overnight.

Cobalt: According to Ledrut and Hauss,[189] a cobalt oxalate of normal composition is obtained by precipitating cobalt with sodium oxalate in 25 per cent formic acid solution.

Procedure: The cobalt solution, which ought to be free from nitrate and ammonium, is diluted to about 100 ml., treated with 35 ml. of formic acid, and precipitated at about 70°C. with a three-fold excess of 2 per cent sodium oxalate solution. After 6–7 hours on the steam bath, the precipitate is washed 2 or 3 times by decantation with 25 ml. of 25 per cent formic acid. Washing is continued on a glass filter crucible of fine porosity until the oxalate is removed, but not more than 100 ml. of wash solution should be used. The crucible is placed in an 800 ml. beaker and the precipitate is dissolved in 100 ml. of 10 per cent sulfuric acid at 70° C. After dilution with 500 ml. of 3.3 per cent sulfuric acid the mixture is titrated at 70°C. with $0.1N$ permanganate.

Notes: (1) If nitrate is present, it partially replaces oxalate in the precipitate and low results are obtained.

(2) Formic acid lowers the solubility of cobalt oxalate and favors precipitation of the normal salt.

(3) Nickel interferes. A method for determination of *nickel* as oxalate has been developed by the same authors.[190]

Lanthanum: According to investigations of Kolthoff and Elmquist[191] the volumetric determination of lanthanum as oxalate is one of the most accurate methods for this element in the absence of interfering substances such as other rare earths, calcium, and zinc.

Procedure: To the lanthanum chloride solution add 50 ml. of saturated aqueous oxalic acid, allow to stand from 10 to 20 hours, and filter. Wash with cool water until no more acid is found upon testing the washings with methyl orange. Dissolve the precipitate in warm dilute sulfuric acid and titrate with permanganate in the usual way.

Notes: (1) For quantitative precipitation a great excess of oxalic acid is necessary. Therefore good precision and accuracy cannot be expected in a back-titration of oxalic acid in the filtrate. The direct titration is capable of giving results accurate to ±0.1 per cent.

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[188] T. Matsumoto, *Japan Analyst*, **3**, 221 (1954).

[189] J. Ledrut and L. Hauss, *Bull. soc. chim. Belges*, **41**, 104 (1932).

[190] J. Ledrut and L. Hauss, *Bull. soc. chim. France*, (5) **4**, 1136 (1937).

[191] I. M. Kolthoff and R. Elmquist, *J. Am. Chem. Soc.*, **53**, 1225, 1232 (1931).

(2) Alkali oxalates should not be used in place of oxalic acid in the precipitation because of their tendency to form double salts with lanthanum oxalate.

(3) It is possible to determine the average atomic weight of the constituents of a dried rare earth oxalate mixture by igniting one portion to oxide and weighing, and on another portion titrating the oxalate.[192]

Thorium: Majer[193] determines thorium by precipitating from 10 ml. of solution which is 1*N* in nitric acid. The solution is heated on the water bath, 5 ml. of saturated oxalic acid solution is added dropwise, and the heating is continued for 1–2 hours. After several hours at room temperature, the precipitate is filtered and washed with dilute nitric acid. The precipitate is dissolved in 2*N* sulfuric acid and titrated with permanganate solution at 90° C.

Other Determinations Based on Precipitation as Oxalate: Methods for the determination of barium,[194] strontium,[195] cerium,[196] lead and silver[197] have been described. The original works should be consulted for details.

Melamine: Steele, Glover, and Hodgson[198] determine melamine by precipitating as the oxalate and titrating with permanganate after dissolving the precipitate in dilute sulfuric acid. Cyanuric acid interferes, but sparingly soluble constituents, e.g., ammeline, ammelide, melam, melem, contaminate the precipitate but do not interfere with the titration. The amounts tested were higher than those likely to be found in practice.

Procedure: Transfer 0.1 g. of sample to a 6 × 1 inch test tube, add 20 ml. of water, and warm until all the solid has dissolved. Cool, transfer to a 50 ml. beaker containing 5 ml. of a freshly prepared solution of oxalic acid in ethanol (20 g. of oxalic acid in 100 ml. of ethanol filtered before use). Complete the transference with 5 ml. of water and cool to below 4 °C. in ice for 30 minutes. Filter on a No. 4 sintered-glass crucible, using the filtrate to assist the transference, and wash 5 times with 5 ml. portions of ethanol, cooled to below 4°C. Dry at 105°C. for 30 minutes to expel the ethanol. Place the crucible in a beaker, add 100 ml. of *N* sulfuric acid, heat to 70°C., and titrate with 0.05*N*

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[192] Cf. W. Gibbs, *Am. Chem. J.*, **15**, 548 (1893); G. L. Barthauer, R. G. Russell, and D. W. Pearce, *Ind. Eng. Chem., Anal. Ed.*, **15**, 548 (1943).

[193] V. Majer, *Chem. Listy*, **44**, 68 (1950).

[194] T. Matsumoto, *Bull. Chem. Soc. Japan*, **25**, 361 (1952).

[195] T. Matsumoto, *Bull. Chem. Soc. Japan*, **25**, 242 (1952); *Chem. Abstr.*, **47**, 7939 (1953).

[196] G. S. Deshmukh, *J. Sci. Research Benares Hindu Univ.*, **1**, 121 (1950–1); *Chem. Abstr.*, **46**, 3449 (1952).

[197] K. Kawagaki, *J. Chem. Soc. Japan (Pure Chem. Sect.)*, **73**, 705 (1952); *Chem. Abstr.*, **47**, 4788 (1953).

[198] J. R. Steele, J. H. Glover, and H. W. Hodgson, *J. Appl. Chem. (London)*, **2**, 296 (1952).

The first reaction is favored by sulfuric acid in a concentration of 1:5 or more. Débordeaux suggested treating the nitrate solution with 4–6 g. of manganous sulfate and 12 ml. of concentrated sulfuric acid in a total volume of 100 ml., then refluxing at 94°C. with an excess of oxalic acid which is subsequently titrated with permanganate. Similar methods were applied for the determination of *chlorate, bromate,* and *iodate.* They are not attractive in principle.

Persulfate: Kempf[207] determined the active oxygen content of persulfates with the aid of oxalic acid, using silver sulfate as a catalyst. To 0.2–0.3 g. of alkali persulfate he added an excess (about 25 ml.) of $0.1N$ oxalic acid and a solution of 0.2 g. of silver sulfate in 20 ml. of 10 per cent sulfuric acid. After heating for 15 minutes on the steam bath he titrated the excess with permanganate. Kurtenacker and Kubina[208] obtained too high results by this method, the deviations amounting to more than 3 per cent in some cases.

Acetic Anhydride: For assaying acetic anhydride, Rosenbaum and Walton[209] make use of a hydrolysis reaction with oxalic acid:

$$(COOH)_2 + (CH_3CO)_2O \longrightarrow CO_2 + CO + 2CH_3COOH$$

The reaction proceeds quantitatively in the presence of pyridine or other tertiary bases such as butidine, collidine, or the picolines, which act as catalysts. About 1 g. of the acetic anhydride is weighed from a weighing pipette into a wide-mouthed glass-stoppered bottle containing about 1 g., accurately weighed, of anhydrous oxalic acid (see Notes). A 2-ml. portion of pyridine, dried over barium oxide and calcium hydride, is added and the bottle is kept cool under a tap for 5 minutes to prevent loss of acetic anhydride by vaporization. It is then warmed to 50° C. for about 10 minutes and the excess oxalic acid is titrated with $0.1N$ permanganate.

Notes: (1) Since anhydrous oxalic acid reacts readily with water to form the dihydrate, the acid used should be handled carefully and weighed rapidly, its active strength being checked against permanganate in each series of analyses. According to Rosenbaum and Walton a little moisture (up to at least 0.3 per cent) is not objectionable, since acetic anhydride reacts more rapidly with oxalic acid than it does with water.

(2) Anhydrous oxalic acid may be prepared by the method of Hultman, Davis, and Clarke,[210] in which the ordinary hydrated acid is refluxed with carbon tetrachloride. The refluxing solvent passes through a separator and is dried over calcium chloride before returning. After the acid becomes anhydrous, it is freed from carbon tetrachloride in a stream of warm, dry air.

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[207] R. Kempf, *Ber.*, 1905, 3963.

[208] A. Kurtenacker and H. Kubina, *Z. anal. Chem.*, **83**, 14 (1931).

[209] C. K. Rosenbaum and J. H. Walton, *J. Am. Chem. Soc.*, **52**, 3366 (1930).

[210] I. N. Hultman, A. W. Davis, and H. T. Clarke, *J. Am. Chem. Soc.*, **43**, 368 (1921).

Other Organic Substances: As was previously mentioned, many organic materials can be oxidized completely by permanganate only when kept in contact with an excess of oxidant for some time. Commonly the acid or alkaline mixture is heated for a specified period. Under these conditions, however, permanganate is likely to undergo some autodecomposition (p. 39), so that the values obtained are not entirely trustworthy. Therefore methods for carrying out the oxidation at room temperature were investigated in the Utrecht Laboratory. The results of these and later studies are given in the following pages.

Generally the oxidation of an organic compound with permanganate proceeds more rapidly in alkaline solution than in acid, but the end product is then likely to be oxalate rather than carbonate. The difficulty is avoided by letting the main reaction take place in alkaline medium, then acidifying and allowing a little time for the oxalate formed to react with permanganate before back-titrating. A fairly large excess of permanganate is needed since part of it is reduced to manganese dioxide and thus becomes unavailable. It is well to allow 25 ml. of $0.1N$ permanganate for 10 ml. of $0.1N$ reductant, the normalities being based on the complete reaction. A glass-stoppered Erlenmeyer flask, thoroughly free from grease, is a suitable vessel. Reagents of the highest purity should be used and blank tests should be run on the reagents and permanganate. The back-titrations are made most simply by the iodometric method.

Several organic substances were tested in this way by Kolthoff.[211] Imhof[212] made a systematic study of more compounds, as shown below.

Procedure: To a suitable quantity of the sample solution add 25–50 ml. of $0.1N$ permanganate and 10 ml. of $4N$ sodium hydroxide. Allow to stand stoppered for 24 hours, then add 25 ml. of $4N$ sulfuric acid and let stand for 2 hours longer. Introduce an excess of potassium iodide and titrate the liberated iodine with $0.1N$ thiosulfate (other methods of back-titration may also be used). For good results, not more than half of the permanganate should remain before addition of iodide.

In Table II are listed the number of oxidizing equivalents required per mole of organic material. The "calculated" values are based, unless otherwise specified, on complete oxidation to carbon dioxide and water; the "found" values are those obtained by Imhof.

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[211] See the earlier German editions of this text.

[212] J. G. Imhof, Thesis, Utrecht, 1932.

TABLE II

Oxidation of Organic Compounds by Permanganate

Compound	Equivalents per mole Calculated	Equivalents per mole Found
Monobasic Aliphatic Acids		
Formic acid[a]	2	2.02
Acetic acid	8	0.00
Acetic acid, chloro	—	0.12
Acetic acid, dichloro	—	0.00
Acetic acid, trichloro	—	0.02
Propionic acid	14	0.06
Butyric acid	20	0.04
Isovaleric acid	26	0.16
Caproic acid	32	0.24
Caprylic acid	44	2.6
Capric acid	56	3.6
Dibasic Aliphatic Acids		
Oxalic acid	2	2.00
Malonic acid	8	6.06
Succinic acid	14	0.02
Glutaric acid	20	0.12
Adipic acid	26	0.08
Pimelic acid	32	0.00
Suberic acid	38	0.12
Azelaic acid	44	0.18
Sebacic acid	50	0.22
Hydroxy, Ketonic, and Unsaturated Aliphatic Acids[b]		
Glycolic acid	6	6.14
Lactic acid	12	12.00
Malic acid	12	11.90
Tartaric acid	10	10.02
Citric acid	18	17.92
Pyruvic acid	10	9.96
Levulinic acid	22	18.42
Fumaric acid	12	11.96
Maleic acid	12	11.82
Aromatic Acids		
Benzoic acid	30	0.02
Salicylic acid	28	28.02
m-Hydroxybenzoic acid	28	27.86
p-Hydroxybenzoic acid	28	27.82
Gallic acid	24	24.1
Mandelic acid	34	9.74
Cinnamic acid	40	10.38
Cinnamic acid[c]	10	
Aliphatic Alcohols		
Methanol	6	5.94
Ethanol	12	7.5
Propyl alcohol	18	7.04
Isopropyl alcohol	18	13.72
Butyl alcohol	24	7.72
Isobutyl alcohol	24	6.40
t-Amyl alcohol	30	0.10
Ethylene glycol	10	9.98
Glycerol	14	14.02
Erythritol	18	18.00
Pentaerythritol	24	23.80
Mannitol	26	26.16
Allyl alcohol	16	15.88
Aldehydes and Ketones		
Paraldehyde[d]	6	6.10
Acetone	16	13.64
2-Butanone	22	14.56
3-Pentanone	28	17.22
Benzophenone	60	0.0
Phenols		
Phenol	28	27.90
o-Cresol	34	28.18
m-Cresol	34	28.18
p-Cresol	34	27.20

TABLE II (*Continued*)

Oxidation of Organic Compounds by Permanganate

Compound	Equivalents per mole		Compound	Equivalents per mole	
	Calculated	Found		Calculated	Found
Phenols (*Continued*)			*Various Nitrogen Compounds*[f]		
Pyrocatechol	26	25.86			
Resorcinol	26	25.86	Methylamine	6	6.02
Hydroquinone	26	25.86	Aniline[g]	28	26.94
Pyrogallol	24	23.40	Acetanilide	28	27.88
Phloroglucinol	24	24.20	Sulfanilic acid	28	27.8
o-Nitrophenol[e]	28	27.52	Urea	0	0.0
m-Nitrophenol[e]	28	28.02	Barbituric acid	8	6.1
p-Nitrophenol[e]	28	27.82	Hydrocyanic acid	2	2.04
Picric acid[e]	28	27.92	Ethyl urethan	12	7.72

[a] See also below.

[b] All hydroxy acids, with the exception of levulinic, are oxidized completely to carbon dioxide and water.

[c] Calculated for oxidation to benzoic acid, carbon dioxide, and water.

[d] Calculated for oxidation to acetic acid.

[e] Oxidation to nitric acid, carbon dioxide and water.

[f] Oxidation to carbon dioxide, ammonia, and water.

[g] Stood 48 hours in alkaline permanganate.

Modifications of the alkaline permanganate method, giving suitable conditions for the oxidation of certain compounds, are given below.

Formic Acid: That formate is smoothly oxidized in alkaline solution was established long ago by St. Gilles.[213] One makes the formic acid solution alkaline with sodium hydroxide or carbonate, pipettes in an excess of permanganate, acidifies after an hour with sulfuric acid, and titrates the excess oxidant. If the mixture is warmed, oxidation takes place in a few minutes.

Molotkova and Zolutkhin[214] state that permanganate is stable only for 1 hour in a sodium carbonate medium. They allow the mixture to stand for 20–30 minutes, acidify with 7*N* sulfuric acid, add a known excess of 0.1N ferrous ammonium sulfate, and titrate back with permanganate.

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[213] L. Péan de St. Gilles, *Ann. chim. et phys.*, (3) 55, 388 (1859). On the influence of the hydrogen-ion concentration see W. H. Hatcher and C. R. West, *Trans. Roy. Soc.* (*London*), 21, 269 (1927); *Chem. Abstr.*, 22, 1518 (1928).

[214] A. S. Molotkova and V. K. Zolutkhin, *Zavodskaya Lab.*, 18, 1284 (1949).

According to Oberhauser and Hensinger,[215] it is possible to titrate formate directly with permanganate if one neutralizes the free acid with sodium carbonate, adds 10–20 ml. of a cool saturated solution of pure sodium acetate (p. 99), and warms the mixture to around 80°C. Hydrated manganese dioxide separates out rapidly and the total reaction time amounts to only about 15 minutes.

Other low molecular weight members of the saturated fatty acid series are not attacked by permanganate, and the method is especially suited for the determination of formic acid in the presence of acetic. Higher fatty acids are somewhat oxidized, although very incompletely (see p. 114). The oxidation of propionic acid to oxalic acid is described on p. 110.

Stamm[216] obtains a rapid reaction by letting the formate solution run into alkaline permanganate to which much barium salt has been added. In this case barium manganate is produced and the normality of the permanganate is the same as the molarity. The procedure is the same as in the Stamm titration of iodide (p. 62).

Citrates, Tartrates, and Salicylates: Zolutkhin and Molotkova[217] studied the influence of inorganic salts on the oxidation of citrates, tartrates, and salicylates using an adaptation of Kolthoff's method. They treated 10 ml. samples (0.2N) with 2–5 ml. of the metal nitrate or sulfate, 25 ml. of 0.2N permanganate, and 10 ml. of 4N sodium hydroxide solution. After varying periods of standing in the dark, 15 ml. of 7N sulfuric acid and an excess of 0.1N ferrous ammonium sulfate were added. The solution was then titrated back with permanganate.

Without catalyst present, oxidation of tartrate was complete in 24 hours, but calcium or copper brought about 99.5 per cent oxidation in 2 hours although copper affected the permanganate titer. Chromium(III) increased the time of oxidation.

With citrate there was 79.16 per cent oxidation after $1^1/_2$ hours and only 79.2 per cent oxidation after 24 hours. Catalysts had no effect; hence it is recommended that an empirical titer be used. With salicylate 99.45 per cent oxidation occurred after 3 hours; catalysts had no effect.

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[215] F. Oberhauser and W. Hensinger, *Z. anorg. u. allgem. Chem.*, **160**, 366 (1927).

[216] H. Stamm, *Z. angew. Chem.*, **47**, 791 (1934).

[217] V. K. Zolutkhin and A. S. Molotkova, *Trudy Komissii Anal. Khim. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, **5** (8), 179 (1954).

Lactic Acid: Ernst and Horváth[218] have described a microdetermination of lactic acid in which the sample in 5 per cent sulfuric acid solution is heated with excess permanganate for 15 minutes on a steam bath and is thereby oxidized to acetic acid. Four equivalents of oxidant are required per mole of lactic acid; 1 ml. of $0.1N$ permanganate corresponds to 2.25 mg. The self-decomposition of permanganate has to be considered and a correction for it is established by oxidizing known quantities of oxalic acid under similar conditions.

A rapid method for the determination of tartaric acid with alkaline permanganate is given by Richert.[219]

Methanol: In alkaline solution at room temperature, methanol is oxidized slowly but completely by permanganate (p. 114). Nanji and Norman[220] gave a more rapid procedure in which the sample is refluxed with alkaline permanganate.

Procedure: Place 100.0 ml. of $0.3N$ permanganate and 40 ml. of sodium hydroxide solution (150 g. of pure NaOH per liter) in a glass-stoppered Erlenmeyer flask and add an amount of sample containing not more than 10 mg. of methanol. Mix, connect to a reflux condenser with a ground-glass joint, heat to boiling over a period of 7–10 minutes, and keep at gentle boiling for 5 minutes. Disconnect the flask and without cooling add 100.0 ml. of oxalic acid (20.0 g. of $H_2C_2O_4 \cdot 2H_2O$ per liter) and 40 ml. of 1:2 sulfuric acid. Titrate the hot solution with $0.05N$ permanganate to a permanent pink end-point. Run a blank in the same way and calculate the amount of methanol from the difference in titrations. For best results the $0.05N$ permanganate should be standardized by running known amounts of methanol. The equivalent weight of methanol in this procedure is close to one sixth of the molecular weight.

Under the conditions given by Nanji and Norman, ethanol consumes 6 equivalents of oxidant per mole and isopropyl alcohol consumed from 17 to 18. Even at room temperature ethanol appears to be oxidized to the same extent during the first 5 minutes. Evidently the reaction is complex, some acetic acid and some oxalic acid being formed.

Methanol can also be determined by Stamm's method (p. 62) in the same way as formate. During titration the temperature of the solution should be 35–40°C.

Formaldehyde: According to Stamm[216] formaldehyde may be determined by the procedure given for formate. Naturally methanol interferes.

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[218] E. Ernst and G. Horváth, *Biochem. Z.*, **224**, 135 (1930).

[219] P. H. Richert, *Ind. Eng. Chem., Anal. Ed.*, **2**, 273 (1930).

[220] D. R. Nanji and A. G. Norman, *J. Soc. Chem. Ind.* (*London*), **45**, 337T (1926).

Ethanol: In acid medium at room temperature the oxidation goes quantitatively to acetic acid:

$$CH_3CH_2OH + 2O \longrightarrow CH_3COOH + H_2O$$

One mixes 10 ml. of 0.1*N* ethanol solution (10–12 mg. of alcohol) with 10 ml. of 4*N* sulfuric acid and 25 ml. of 0.1*N* permanganate, allows the mixture to stand 24 hours, and determines the excess permanganate.

Under the same circumstances *n*-propyl alcohol is oxidized to propionic acid.

Pyramidone: Under carefully controlled conditions, pyramidone (4-dimethylamino-1,5-dimethyl-2-phenyl-3-pyrazolone) can be oxidized by alkaline permanganate in such a way that it consumes 4 equivalents of oxidant per mole. Schulek and Menyhárth[221] gave the following directions.

Procedure: A sample containing 0.3–0.5 g. of finely divided pyramidone is made up to 100 ml. with water in a volumetric flask. A 10 ml. aliquot, filtered if necessary, is diluted to 350 ml. and treated with 0.1*N* sodium hydroxide in an amount about equal to the calculated volume of 0.1*N* permanganate later required. Mix well, introduce an excess of permanganate, mix again, and rapidly add 1 g. of potassium iodide. After thorough shaking add 10 ml. of 1:2 sulfuric acid and titrate with 0.1*N* thiosulfate to a weak yellow-green color. Add starch indicator and complete the titration to a point at which the blue color does not return within a minute, the mixture again being shaken well in the meantime. Determine the permanganate titer in a blank test on the same amount.

Notes: (1) For every 10 mg. of pyramidone at least 5 ml. of permanganate should be added. The latter should not be put in dropwise, but rather from a pipette with a fairly large opening. Each milliliter of 0.1*N* permanganate consumed corresponds to 5.78 mg. of pyramidone.

(2) Quinine, salicylic acid, sugars, and starches interfere, but phenacetin, acetanilide, adalin, veronal, luminal, caffeine, camphoric, citric, and acetylsalicylic acids, antipyrine, and atophan may be present. Pyramidone can be extracted from sugars and starches (and from alkaline solutions of interfering acids) with chloroform; the latter is carefully evaporated and the residue analyzed as above.

Other Substances: The sugars glucose, levulose, lactose, and sucrose can be oxidized as well in acid as in alkaline solution but do not go completely to carbon dioxide and water. Apparently a little acetic acid is formed also, the underconsumption of permanganate amounting to 3 or 4 per cent, depending upon the kind of sugar.

In adsorption studies Kolthoff has made use of the room temperature oxidation of alkaloids with acid permanganate. The method is empirical, so a known quantity of the alkaloid in question should be run as a standard under identical conditions. Ten milliliters of $0.001M$ morphine solution, for example, consumed 6.5 ml. of $0.1N$ permanganate in 24 hours.

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[221] E. Schulek and P. Menyhárth, *Z. anal. Chem.*, 89, 426 (1932).

Aconitic acid and itaconic acid can be determined by titrating in an acid medium with permanganate at the boiling point.[222] The permanganate must, however, be standardized empirically. When both substances are present together, aconitic acid is separated by precipitating with saturated mercurous nitrate solution. Itaconic acid in the filtrate is titrated after removal of the excess of mercurous ion with hydrochloric acid.

Evans[223] demonstrated that in neutral permanganate at 50 or 75°C. propylene glycol is converted quantitatively to acetic acid and carbon dioxide. Fries and Calvin[224] studied the reaction between permanganate and propene with the aid of radioactive carbon. Both acetic acid and carbon dioxide were formed, the latter predominating in alkaline solution, but some oxalic acid was produced also. The acetic acid was shown to be derived from the $CH_3—CH=$ portion of the propene molecule.

In a study of the potential of the permanganate-cyanide pair in alkaline solution, Gauguin[225] observed that cyanogen is formed at pH values below 13, whereas cyanate appears at greater alkalinity. The formation of cyanate is irreversible.

Permanganate is used for the determination of reducing substances in paper, water, and various products. The permanganate number of paper pulp is defined as the number of milliliters of $0.1N$ permanganate consumed by 1 g. of oven-dried pulp under carefully controlled conditions,[226] and to some extent serves to indicate the bleach requirement of the pulp.[227]

[222] K. Lauer and S. M. Makar, *Anal. Chem.*, **23**, 587 (1951).

[223] W. L. Evans, *J. Am. Chem. Soc.*, **45**, 171 (1923).

[224] B. A. Fries and M. Calvin, *J. Am. Chem. Soc.*, **70**, 2235 (1948).

[225] R. Gauguin, *Bull. soc. chim. France*, **1948**, 1048.

[226] R. H. Wiles, *Paper Trade J.*, **98**, No. 11, 34 (1934).

[227] Cf. R. Bourgon, *Pulp & Paper Mag. Can.*, **47**, No. 3, 125 (1946).

CHAPTER IV

OXIDIMETRY WITH CERIC SALTS

1. Ceric Sulfate as a Volumetric Reagent. The use of ceric salts as volumetric reagents was first proposed about the middle of the last century,[1] but the first systematic studies were not undertaken until some 70 years later when Willard and Young began their work in this field.[2] At about the same time Furman,[3] Atanasiu,[4] and their collaborators described various potentiometric methods using ceric sulfate as titrant. As a result of these and later investigations, ceric solutions have assumed considerable importance in oxidimetry. A comprehensive review of the subject has been given by Young.[5]

Tetravalent cerium in acid solution is a strong oxidant (see below); its reduction proceeds directly to trivalent cerium by a reversible one-electron reaction.

$$Ce^{4+} + e \rightleftharpoons Ce^{3+}$$

In this respect ceric cerium has many advantages over permanganate and dichromate. In the reduction of these oxidizing agents, intermediate unstable valence states are formed; these may give rise to induced oxidation of reducing agents which do not react, or react very slowly, with permanganate and dichromate. For example, the titration of ferrous iron with dichromate gives rise to the induced oxidation of many organic substances which might be present in the solution. On the other hand, such an induced oxidation does not occur in the titration of ferrous iron with ceric sulfate in the presence of a large number of organic compounds (e.g., alcohols). Furthermore, hydrochloric acid does not interfere in most applications and ceric sulfate solutions are very stable; in these respects permanganate is far inferior. Phosphoric acid interferes at low acidity because of precipitation of ceric phosphate; the precipitate dissolves if the acid concentration is greater than 1*N*.

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[1] L. T. Lange, *J. prakt. Chem.*, **82**, 129 (1861); F. L. Sonnenschein, *Ber.*, **3**, 631 (1870); A. Job, *Compt. rend.*, **128**, 101 (1899); G. Barbieri, *Chem. Ztg.*, **29**, 668 (1905); F. Sommer and H Pincas, *Ber.*, **48**, 1963 (1915); J. Martin, *J. Am. Chem. Soc.*, **49**, 2133 (1927). The oxidation of organic compounds was studied by A. Benrath and K. Ruland, *Z. anorg. u. allgem. Chem.*, **114**, 267 (1920).

[2] H. H. Willard and P. Young, *J. Am. Chem. Soc.*, **50**, 1322, 1334, 1368, 1372, 1379 (1928); **51**, 139, 149 (1929).

[3] N. H. Furman, *J. Am. Chem. Soc.*, **50**, 755 (1928); N. H. Furman and O. M. Evans, *ibid.*, **51**, 1129 (1929); N. H. Furman and J. H. Wallace, *ibid.*, **52**, 1443, 2346 (1930).

[4] J. A. Atanasiu, *Bull. Chim. Soc. Române Chim.*, **30**, 73 (1927); *Chem. Abstr.*, **22**, 2900 (1928); J. A. Atanasiu and V. Stefanescu, *Ber.*, **61**, 1343 (1928).

[5] P. Young, *Anal. Chem.*, **24**, 152 (1952); cf. W. Petzold, *Die Cerimetrie und die Anwendung der Ferroine als massanalytische Redoxindikatoren*, Verlag Chemie, Weinheim/Bergstrasse, 1955.

The oxidation potential of the ceric-cerium system depends on the acidity and particularly on the kinds of anions present. In perchloric acid no complex is formed;[6] in other acids the ceric cerium may form complexes with the corresponding anions.[7] The oxidation potentials of the system at different concentrations of various acids are listed in Table I.

TABLE I

Acid normality	Oxidation potentials vs. normal hydrogen electrode			
	$HClO_4$	HNO_3	H_2SO_4	HCl
1	1.70	1.61	1.44	1.28
2	1.71	1.62	1.44	
4	1.75	1.61	1.43	
8	1.87	1.56	1.42	

On the basis of this evidence, Smith and Getz[7] concluded that the oxidizing action of a ceric solution is a function of the cerate-ion concentration; therefore they make use of the term *cerate oxidimetry.* The present authors prefer to consider that any form of tetravalent cerium may serve as an active oxidant.

Chloride and sulfate form complexes with ceric ions. Fluoride forms a very stable complex with ceric cerium and lowers the oxidation potential of the system considerably. Ceric salts are strongly hydrolyzed and ceric hydroxide (hydrous ceric oxide) precipitates at relatively low pH. Titrations with ceric cerium therefore must be carried out in relatively strong acid medium. The ceric hydroxide can be kept in solution by strong complex formers but such complexes, e.g., of pyrophosphate or ethylenediaminetetraacetate, are very poor oxidizing agents.

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[6] Cf. E. L. King and M. L. Pandow, *J. Am. Chem. Soc.,* **74,** 1966 (1952).

[7] G. F. Smith and C. A. Getz, *Ind. Eng. Chem., Anal. Ed.,* **10,** 191 (1938); cf. E. G. Jones and F. G. Soper, *J. Chem. Soc.,* **1935,** 802.

Detection of the End-Point: Certain titrations, such as those of oxalic acid and hydrogen peroxide, can be done without an indicator provided that fairly large amounts are present and an appropriate blank correction is made. It is better, however, to use an indicator when possible.

In most of the early methods in which ceric sulfate was used, the end-point was detected potentiometrically, but visual indicators were described for certain determinations. For example, Willard and Young[8] recommended methylene blue in the titration of oxalate in the presence of iodine monochloride catalyst, and diphenylamine or diphenylbenzidine in the titration of ferrous iron after a stannous chloride reduction;[9] phosphoric acid had to be added with these latter indicators. Diphenylaminesulfonic acid[10] and diphenylbenzidinesulfonic acid[11] may also be used in the titration of ferrous iron, preferably in the presence of phosphoric acid. For further details of the diphenylamine indicators, see p. 170 and Vol. I, p. 133. Hammett *et al.*[12] prepared *p*-nitrodiphenylamine which has an oxidation potential 0.3 v. higher than the parent base; this indicator gave satisfactory end-points in titrations with ceric cerium. Various amino derivatives of diphenylamine have also been prepared.[12]

Rathsburg[13] titrated antimony(III) with methyl red, methyl orange, congo red, or methylene blue as indicator, the dyestuff being irreversibly oxidized at the end-point. Furman and Wallace[14] used diphenylamine or methyl red in the titration of hydroquinone, and methyl red, erioglaucine A, or eriogreen B in the titration of ferrous iron. The last two indicators had been previously recommended for titrations with permanganate by Knop.[15,16]

Several other triphenylmethane dyes were studied by Knop and Kubelkova (cf. p. 25) and were found suitable as indicators in cerimetry, but only certain of these have found even a limited use. These are the two referred to above together with setoglaucine O and xylene cyanol FF. Further details of these indicators are given in Vol. I.[17,18]

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[8] H. H. Willard and P. Young, *J. Am. Chem. Soc.*, 50, 1322 (1928).

[9] *Idem, ibid.*, 1334.

[10] L. A. Sarver and I. M. Kolthoff, *J. Am. Chem. Soc.*, 53, 2902 (1931).

[11] L. A. Sarver and W. von Fischer, *Ind. Eng. Chem., Anal. Ed.*, 7, 271 (1935).

[12] L. P. Hammett, G. H. Walden, and S. M. Edmonds, *J. Am. Chem. Soc.*, 56, 1092 (1934).

[13] H. Rathsburg, *Ber.*, 61, 1663 (1928).

[14] N. H. Furman and J. H. Wallace, *J. Am. Chem. Soc.*, 52, 1443 (1930).

[15] J. Knop, *J. Am. Chem. Soc.*, 46, 263 (1924).

[16] J. Knop and O. Kubelkova, *Z. anal. Chem.*, 77, 125 (1929); 85, 401 (1931).

After Kunz[19] had made the first careful measurement of the potential of the ceric-cerous system in 1931 and had shown it to be 1.44 v. in 1.0*M* sulfuric acid, it was realized that diphenylamine and its sulfonic acid did not possess sufficiently high redox potentials to be entirely satisfactory for cerimetric titrations. A more suitable indicator was discovered by Walden, Hammett, and Chapman,[20] ferrous *o*-phenanthroline (ferroin), which has a molar oxidation potential of 1.14 v. In a more recent paper, Kolthoff and Hume[21] reported the formal oxidation potential as 1.06 v. In its reduced form the indicator is deep red, and in the oxidized form it is pale blue. No phosphoric acid need be added and the indicator blank is negligible with 0.1*N* solutions; the indicator solution is very stable. Ferroin is the indicator most generally used in titrations with ceric sulfate.

Various other indicators have been studied for cerimetric titrations. Hammett, Walden, and Edmonds[22] prepared nitrophenanthroline (nitroferroin) which has a potential of 1.25 v. It is more stable than ferroin and, unlike the latter, is not oxidized in *M* sulfuric acid solutions containing vanadate. However, it is unsatisfactory when used in the titration of ferrous iron with ceric sulfate, for a significant excess of titrant is required to oxidize the indicator; this is to be

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[17] Cf. R. N. Adams and E. M. Hammaker, *Anal. Chem.*, **23**, 744 (1951)(alphazurine G); H. M. Tomlinson, O. T. Aepli, and H. M. Ebert, *ibid.*, 287 (xylene cyanol FF); B. F. Miller, and D. D. Van Slyke, *J. Biol. Chem.*, **114**, 583 (1936) (setopaline C).

[18] There seems to be confusion about several of these indicators. Adams and Hammaker refer to alphazurine G in such a way as to imply that it is a different dyestuff from patent blue V (Vol. I, p. 139). Both of these have a *C.I.* No. of 712 and are the same as disulphine blue V. Tomíček (*Chemical Indicators*, Butterworths, London, 1951) states that erioglaucine is the same as alphazurine G, but the *C.I.* numbers are different; erioglaucine and alphazurine FG have the same *C.I.* number, 671. Setopaline C is probably the same dyestuff as setocyanine, *C.I.* 663.

[19] A. H. Kunz, *J. Am. Chem. Soc.*, **53**, 98 (1931).

[20] G. H. Walden, L. P. Hammett, and R. P. Chapman, *J. Am. Chem. Soc.*, **53**, 3908 (1931); **55**, 2649 (1933); cf. G. H. Walden and S. M. Edmonds, *Chem. Rev.* **16**, 81 (1935); G. F. Smith and C. A. Getz, *Ind. Eng. Chem., Anal. Ed.* **10**, 304 (1938).

[21] I. M. Kolthoff and D. N. Hume, *J. Am. Chem. Soc.*, **65**, 1895 (1943).

[22] L. P. Hammett, G. H. Walden, and S. M. Edmonds, *J. Am. Chem. Soc.*, **56**, 1092 (1934).

expected in view of the high oxidation potential of the indicator. Nevertheless, nitroferroin is very useful for titrations with ceric ions in a perchloric acid medium where the potential is higher (p. 122).

Smith and Richter[23] prepared a number of substituted *o*-phenanthrolines (ferroins) and determined the redox potentials in various concentrations of sulfuric acid. Their values, together with those of ferroin itself and of 2,2′-dipyridyl for comparison, are given in Table II.

TABLE II

Molar Oxidation Potentials of Ferroin and Substituted Ferroins

	Sulfuric acid concn. with corresp. E^0 in volts:						
Indicator as Fe^{2+} complex	0.5*M*	1*M*	2*M*	3*M*	4*M*	6*M*	8*M*
5-Nitro-(1,10)-phenanthroline	1.26	1.25	1.22	—	1.17	1.12	1.01
5-Methyl-6-nitro-(1,10)-phenanthroline	—	1.23	—	—	—	—	—
5-Bromo-(1,10)-phenanthroline	1.13	1.12	—	—	—	—	—
5-Chloro-(1,10)-phenanthroline	—	1.12	1.10	—	1.04	0.97	—
(1,10)-Phenanthroline	—	1.06	1.03	1.00	0.96	0.89	0.76
5-Methyl-(1,10)-phenanthroline	—	1.02	1.00	0.96	0.93	0.86	0.70
2,2′-Dipyridyl	—	0.97	—	—	0.92	—	—

5-Nitrophenanthroline is useful in titrations with ceric nitrate in nitric or perchloric acid medium; its use is discussed more fully on p. 134. None of the other substituted compounds which are listed in Table II has found any application.

In a further paper, Brandt and Smith[24] have described the preparation and properties of 22 new methyl-substituted phenanthrolines. The oxidation potentials of the series varied from 0.84 to 1.10 v. (1,10-phenanthroline) in 0.1*M* acid; only a few determinations were made at an acid concentration of 1*M*. The interesting feature of this work was the specific and additive effect of methyl substitution. Substitution in the 3 or 8 position lowered the value by 0.03 v.; in the 5 or 6 position by 0.04 v.; and in the 4 and 7 position by 0.11 v. The influence of methyl substitution on the wave length of maximum absorption was also additive. Hence it should be possible to synthesize indicators of this type with a desired potential. As far as is known, none of these compounds has yet found any practical application as an indicator.

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[23] G. F. Smith and F. P. Richter, *Ind. Eng. Chem., Anal. Ed.*, 16, 580 (1944).

[24] W. W. Brandt and G. F. Smith, *Anal. Chem.*, 21, 1313 (1949).

Walden *et al.*[20] examined 2,2′-dipyridyl but considered it less satisfactory than ferroin because of its more rapid decomposition in acid solution. Cagle and Smith,[25] however, obtained satisfactory results with it in the titration of ferrous iron with ceric sulfate in M hydrochloric or sulfuric acid, despite the fact that its oxidized form is less stable than the reduced form in mineral acid solution. For example, 1.0 ml. of $0.1N$ ceric sulfate was added in excess after the equivalence point had been reached and the solution was then stirred for 5 minutes. When excess of ferrous iron was added, the color of the indicator was restored to its original intensity. When 1 drop of ceric sulfate solution was added in excess and the solution was stirred for 2 hours, the indicator was destroyed. Cagle and Smith suggested that this relative instability may be due to dissociation of the ferric form of the indicator, recombination failing to take place when ferrous iron is again added in excess because of the low pH of the solution. They consider it less likely that addition products of 2,2′-dipyridyl, which fail to react with ferrous iron, are formed because of the well-known stability of the pyridine ring. The applications of this indicator are discussed further on p. 147.

Steigman, Birnbaum, and Edmonds[26] examined the indicator properties of ruthenium 2,2′-dipyridyl. The ruthenous (reduced form) complex is yellow and the ruthenic complex is colorless at the concentrations used for indicators. Both forms are more stable than the corresponding iron complexes with 2,2′-dipyridyl. The formal oxidation potential of the indicator is 1.25 v.;[21] hence it would not be expected to be satisfactory for ceric sulfate titrations, and this was confirmed by the experimental results. However, with ceric solutions of higher potential, e.g., ceric nitrate in nitric or perchloric acid solutions, excellent results were obtained. Thus sodium oxalate in a $2M$ perchloric acid solution was titrated with ceric nitrate solution at room temperature (p. 159). The standardization of ceric solutions by this means was as accurate as by the conventional methods.

N-Phenylanthranilic acid (*o*-diphenylaminecarboxylic acid) is one of the most useful indicators alternative to ferroin for ceric sulfate titrations; it was first proposed by Syrokomskii and Stiepin.[27] The indicator is colorless in the reduced form and pink in the oxidized form; the presence of phosphoric acid is unnecessary (as with ferroin) when ferrous iron is titrated. The cost of the indicator is relatively low. It is claimed that the oxidation potential is 1.08 v.,[27] but this seems unlikely because the indicator has been recommended for titrations with dichromate under conditions where ferroin does not give a good end-point owing to its high oxidation potential (cf. p. 173). The oxidation potential of *N*-phenylanthranilic acid would certainly be expected to be smaller than 1.08 v.

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[25] F. W. Cagle and G. F. Smith, *Anal. Chem.*, **19**, 384 (1947).

[26] J. Steigman, N. Birnbaum, and S. M. Edmonds, *Ind. Eng. Chem., Anal. Ed.*, **14**, 30 (1942); cf. F. H. Burstall, *J. Chem. Soc.*, **139**, 173 (1936).

Other indicators of less importance have been suggested at various times, but these are not likely to supplant ferroin or even *N*-phenylanthranilic acid. Some of these have already been considered in Vol. I. More recent are crystal violet,[28] rhodamine 6G,[29] *N,N'*-tetramethylbenzidine (recommended for titration at elevated temperatures) and its sulfonic acid,[30] and siloxene.[31] The last indicator has chemiluminescent properties; the titration is done in the dark, and light is emitted as soon as the oxidant is present in slight excess. Highly colored ions, e.g., cobalt, do not interfere with this method of end-point detection in the titration of ferrous iron with ceric sulfate.

Stock Solutions of Frequently Used Indicators. *Ferroin:* Dissolve 1.485 g. of the base in 100 ml. of water containing 0.695 g. of ferrous sulfate heptahydrate. This gives a 0.025*M* solution.

Nitroferroin and 2,2'-Dipyridyl: Prepare as with ferroin but use 1.689 g. and 1.17 g. of the base, respectively. Sometimes sparingly soluble dipyridyl ferrous perchlorate, which is obtainable commercially, is used as a saturated aqueous solution.

N-Phenylanthranilic acid: See p. 175.

Diphenylaminesulfonic acid: Prepare a 0.2 per cent aqueous solution of the sodium salt.

Triphenylmethane dyestuffs: Dissolve 0.1 g. in 100 ml. of water.

Indicator Corrections: With the ferroin and dipyridyl indicators a correction of 0.02 ml. of 0.1*N* ceric sulfate is generally deducted for the one drop of indicator added (Table III). The same correction is deducted for 1 ml. of the dipyridyl ferrous perchlorate indicator. With the triphenylmethane dyestuffs, 0.02–0.03 ml. of 0.1*N* ceric sulfate is deducted for each 0.5 ml. of indicator used.

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[27] V. S. Syrokomskii and V. V. Stiepin, *J. Am. Chem. Soc.*, 58, 928 (1936); *Zavodskaya Lab.*, 5, 144 (1936).

[28] T. K. S. Murthy and B. S. V. R. Rao, *J. Indian Chem. Soc.*, 27, 37 (1950); cf. J. P. Watson, *Analyst*, 76, 177 (1951).

[29] B. S. V. R. Rao, *Current Sci. (India)*, 16, 378 (1947).

[30] R. N. Adams and E. M. Hammaker, *Anal. Chem.*, 23, 744 (1951).

[31] F. Kenny and R. B. Kurtz, *Anal. Chem.*, 22, 693 (1950).

TABLE III

Indicators for Ceric Titrations

	E^0 value	Amt. per titration	Color change	
Indicator			Reduced	Oxidized
Nitroferroin	1.25	1 drop	Red	Pale blue
Ferroin	1.06	1 drop	Red	Pale blue
Eriogreen[a]	1.01	0.5 ml.	Yellow	Orange
Erioglaucine[b]	1.01	0.5 ml.	Green	Rose
Setoglaucine[c]	1.00	0.5 ml.	Yellow-green	Yellow-red
Xylene cyanol FF[d]	1.00	0.5 ml.	Yellow	Rose
2,2′-Dipyridyl	0.97	1 drop	Red	Pale blue
N-Phenylanthranilic acid	1.08[e]	3–5 drops	Colorless	Pink
Diphenylaminesulfonic acid	0.85	7–10 drops	Colorless	Red-violet

C.I. 735. [b] *C.I.* 671. [c] *C.I.* 658. [d] *C.I.* 715. [e] Cf. p. 127.

It is important, however, to check the corrections of all indicators under the conditions in which they are used. For example, if the triphenylmethane dyestuffs are not added until the end-point is near, the correction is negligible.

Other properties of the more important indicators are summarized in Table III.

Preparation of Stock Solutions: Although spectroscopically pure cerium salts have been relatively expensive, and in earlier days not always available, it has long been possible to obtain commercial cerous oxalate at moderate prices. Willard and Young[2] as well as others (Barbieri,[1] Furman[3]) have shown that the rare earth elements usually present in trade products do not cause interference. Even traces of iron and phosphates are not objectionable for most purposes.

Cerous oxalate is converted into cerium dioxide, CeO_2, by heating at 600–625 °C. The oxide can then be partially dissolved by digestion with 18*N* (1:1) sulfuric acid. Enough of the acid is taken to give a 1*N* or 2*N* solution on subsequent dilution, and the mixture is heated at 125–130° with mechanical stirring until the undissolved portion appears bright yellow. The solution is next cooled slightly, diluted to an oxidizing normality of about 0.1, heated for an hour at 75–85 °C., and filtered. The undissolved residue can be saved for reextraction when more reagent is needed.

Heinerth[32] preferred to heat ceric ammonium nitrate to fumes with concentrated sulfuric acid, pour off the excess, dissolve the reaction product in water, and dilute with *N* sulfuric acid to the desired strength. This process avoids the tedious filtration to remove ceric oxide, which quickly clogs the pores of the filter.

[32] E. Heinerth, *Z. Elektrochem.*, **37**, 62 (1931).

The stability of ceric sulfate solution has been proved by Willard and Young,[2] who kept a $0.1N$ solution (N in sulfuric acid) for nearly a year without change in titer. Similar results have been obtained by Furman and by the authors. Moreover, an acidified ceric sulfate solution free from reducing substances can stand prolonged boiling without losing its oxidizing strength.

Smith, Sullivan, and Frank[33] have described the preparation of pure ceric ammonium nitrate (ammonium hexanitratocerate). This material is commercially available, and after being dried for 4–6 hours at 85°C. it can be used directy for preparing standard solutions, as noted hereafter. Heating at higher temperatures or for a longer time at 85°C. causes some decomposition.[34] Solutions of the nitrate in $2N$ sulfuric acid or $1\text{-}3N$ nitric acid are stable, but solutions in N perchloric acid diminish gradually in titer and should be restandardized after 3 days. Storage in dark bottles in a cool place is recommended. Smith and Fly[34] give essentially the following directions for making up $0.1N$ solutions in N perchloric or $2N$ sulfuric acid.

Place 54.826 g. of the dried salt in a 1 liter beaker and add 83.8 ml. of 72 per cent perchloric acid. The salt will not dissolve, but the mixture should be stirred for 2 minutes. Successively add five 100 ml. portions of water, stirring for 2 minutes after each addition. When the material is completely dissolved, dilute to 1 liter in a volumetric flask and mix.

To prepare a sulfuric acid solution use 56 ml. of 95 per cent sulfuric acid in place of the perchloric and proceed in the same manner with one exception: add the first 100 ml. of water gradually over a period of 5 minutes, with stirring. If these precautions are not taken, mixed salts will precipitate on standing.

Solutions prepared as above contain ammonium and nitrate ions which may be objectionable for some purposes. To prepare a ceric sulfate solution free from these ions, a weighed sample of the nitrate is dissolved and the cerium is precipitated as ceric hydroxide with ammonia, filtered on a fine porosity glass filter, washed, and dissolved in the required quantity of warm $2\text{–}4N$ sulfuric acid. Contact with filter paper or platinum sponge should be guarded against since the ceric ions are in part reduced by these materials. Protection of perchloric acid–ceric solution from traces of reducing substances is particularly important because of the high oxidation potential of the reagent. Dust, impure water, and too much grease on burette stopcocks should be avoided.

In a more recent paper, Smith[35] has described a preparation of ceric perchlorate in which ceric ammonium nitrate is used as starting material. Nitrates are eliminated during the process. The salt is heated with perchloric acid and hydrogen peroxide to reduce it to the trivalent stage, then it is taken to fumes of perchloric acid and it is finally converted to ceric perchlorate by electrolytic oxidation. This solution is stored in an ice box until ready for use, when it is diluted to the approximate concentration required; it is standardized against sodium oxalate (p. 134).

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[33] G. F. Smith, V. R. Sullivan, and G. Frank, *Ind. Eng. Chem., Anal. Ed.*, **8**, 449 (1936); G. F. Smith and C. A. Getz, *ibid.*, **12**, 339 (1940); cf. R. J. Meyer and R. Jacoby, *Z. anorg. Chem.*, **27**, 359 (1901).

[34] G. F. Smith and W. H. Fly, *Anal. Chem.*, 21, 1233 (1949).

[35] G. F. Smith, *Anal. Chem.*, **27**, 1144 (1955).

A method has been described for recovering ceric oxide from titration residues.[36] Even under unfavorable circumstances, the recovery is generally greater than 95 per cent.

Standard Substances. *(a) Ceric Ammonium Nitrate* ($(NH_4)_2Ce(NO_3)_6$; equivalent weight, 548.26; rational, 548.0): The use of this salt for making up ceric solutions is described above. Smith and Fly[34] investigated its properties as a standard substance and proposed the following purity tests:

Insoluble Matter: Dissolve 5.5 g. of the salt in the smallest possible volume of water at room temperature. The saturated solution obtained should be sparkling clear and red in color, with no insoluble material. A 1.0 g. sample of the salt should be completely soluble in 75 ml. of absolute ethanol.

Iron: To the above saturated aqueous solution add 30 per cent hydrogen peroxide dropwise with constant stirring until the orange color is almost gone. Complete the reduction of cerium(IV) by dropwise addition of 3 per cent peroxide and add 0.5 g. of hydroxylamine hydrochloride to reduce any iron. Neutralize to a pH of about 5 with dilute ammonia, as shown by spotting on an indicator paper (Smith and Fly used congo red paper). Complex the ferrous iron with 5 ml. of saturated, aqueous 1,10-phenanthroline and compare the color formed with a blank and with standards containing known quantities of iron. Sensitivity, 0.0002 per cent.

Ignition Residue. Weigh accurately a sample of about 1 g. in an ignited and tared porcelain crucible. Decompose the salt by heating gradually over a very low flame and finally ignite to constant weight at 900°C. The residue from pure ceric ammonium nitrate should amount to 31.396 per cent of the original weight.

Smith and Fly[34] found the active strengths of two primary standard grade products to average 99.98 per cent of the theoretical, with variations over a range of 99.95–100.03 per cent, in titrations of standard arsenic trioxide and sodium oxalate.

Other ceric solutions, such as the sulfate, may be standardized by comparing their oxidizing titers with that of a standard ceric ammonium nitrate solution, against portions of the same ferrous solution. Diphenylaminesulfonate or ferroin can be used as indicator.

(b) Bis-ethylenediammonium Ceric Sulfate ($(Ce(NH_3{-}CH_2{-}CH_2{-}NH_3)_2)(SO_4)_4 \cdot 7H_2O$; equivalent weight, 774.7; rational, 774.27):

Recently Singh and Singh[37] have proposed that this salt be used as a standard substance for the preparation of ceric solutions. It is said not to effloresce or deliquesce and to be stable indefinitely; its solution may be heated to boiling without decomposition. A $0.02N$ standard solution is prepared by dissolving the appropriate amount in $2N$ sulfuric acid. The salt is insufficiently soluble for $0.1N$ solutions to be prepared; hence its use would be limited to microdeterminations.

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[36] F. R. Duke and K. G. Stone, *Ind. Eng. Chem., Anal. Ed.*, **16**, 721 (1944).

[37] B. Singh and S. Singh, *Anal. Chim. Acta*, **14**, 109 (1956).

Critical studies of this substance would be necessary before it could be recommended as a standard.

2. Standardization of Ceric Solutions. ***(a) With Arsenic Trioxide:*** The simplest standardization of ceric sulfate solution is against arsenic trioxide; for properties and purity tests of this primary standard, see p. 41. In dilute sulfuric acid, ceric ion reacts scarcely at all with arsenite. It is even possible to titrate ferrous iron with ceric sulfate without interference from arsenious acid; this cannot be done conveniently with permanganate. However, Gleu[38] pointed out that arsenite is oxidized quite rapidly by a ceric solution if a trace of osmium tetroxide (osmic acid) is added, and that ferrous 1,10-phenanthroline can be used as indicator,[39] giving a sharp endpoint.

Procedure: Dissolve the weighed arsenic trioxide, 0.15 g. for about 30 ml. of $0.1N$ ceric solution, in 10 ml. of N sodium hydroxide. When it has dissolved, add 50 ml. of N sulfuric acid, 3 drops of $0.01M$ (0.25 per cent) osmium tetroxide solution in $0.1N$ sulfuric acid, and 1 or 2 drops of $0.01M$ ferroin indicator (p. 127). Titrate with ceric solution until the red color disappears. The oxidant should be added very slowly near the end.

Notes: (1) A standard solution of arsenic trioxide may be used, but one that contains chloride should be avoided since hydrochloric acid interferes. Gleu suggested adding mercuric perchlorate to overcome the interference.

(2) Gleu obtained good agreement between single standardizations of a $0.1N$ solution against arsenite and oxalate. Smith[40] presented data showing agreement between standardizations of $0.05N$ ceric sulfate and ceric nitrate solutions against arsenite, oxalate, and iron, as well as of $0.01N$ ceric sulfate against arsenite and oxalate.

(3) It is noteworthy that the oxidized (ferric) form of the indicator is not reduced by arsenious acid alone. In the presence of osmium catalyst only a faint red color is developed. As soon as a drop of ceric solution is added, however, the deep red of ferrous phenanthroline appears. Apparently the ceric-arsenite reaction induces the reduction of ferroin by arsenite.

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[38] K. Gleu, *Z. anal. Chem.*, **95**, 305 (1933).

[39] Cf. G. H. Walden, Jr., L. P. Hammett, and R. P. Chapman, *J. Am. Chem. Soc.*, **55**, 2649 (1933).

[40] G. F. Smith, *Cerate Oxidimetry*, Smith Chemical Co., Columbus, Ohio, 1942, pp. 35, 41. Attention may be drawn to a misprint in Smith's directions for preparation of $0.1N$ arsenite, pp. 39 and 41, specifying 3.074 instead of 4.943 g. of As_2O_3 per liter.

Iodine chloride can also serve as the reaction catalyst, as was shown by Willard and Young.[41] End-point indication may be provided at room temperature by the color of iodine in carbon tetrachloride or, at 50°C., by the ferrous phenanthroline complex.[42] Titers about 0.3 per cent low were found with the iodine chloride method at first, but Swift and Gregory[43] were able to obtain excellent results by titrating in $4M$ hydrochloric acid. Willard and Young[42] demonstrated that the concentration of chloride ions is more critical than the concentration of hydrogen ions, and that the reaction is quantitative and rapid in a $3.4M$ chloride solution, which is $1.2M$ in acid, as well as in a 3.0–$4.2M$ solution of hydrochloric acid.

The iodine chloride solution used as a catalyst is prepared by adding 25 ml. of $0.04M$ potassium iodide and 40 ml. of $12M$ hydrochloric acid to 20 ml. of $0.025M$ potassium iodate. Several milliliters of carbon tetrachloride are added and the mixture is titrated with either iodate or iodide, as needed, until a barely perceptible iodine color remains in the organic solvent after shaking and settling. The aqueous phase is considered to be about $0.017M$ in iodine chloride.

Procedure with Ferroin:[42] Place the appropriate quantity of standard arsenite solution (p. 43) in a 400 ml. beaker, add 25 ml. of $12M$ hydrochloric acid and 1 ml. of $0.017M$ iodine chloride, and dilute to about 80 ml. Add 2–3 drops of $0.01M$ ferroin indicator and titrate at room temperature with ceric sulfate until the brown color of the solution returns slowly after the addition of each drop. Heat to 50°C. and continue the titration slowly until there is no return of the brown color within one minute.

Procedure with Carbon Tetrachloride.[41] Pipette the arsenite solution into a 250 ml. glass-stoppered Erlenmeyer flask and add sufficient $12M$ hydrochloric acid to make the acid concentration $4M$ at the end-point. Introduce 3–4 ml. of carbon tetrachloride and 5 ml. of $0.017M$ iodine chloride solution, then titrate with the ceric sulfate, shaking well between additions, until no iodine color remains in the carbon tetrachloride. The shaking must be especially vigorous near the end-point.

(b) Standardization against Oxalate: Willard and Young[2] employed sodium oxalate as a standard substance for ceric solutions. For the preparation and testing of this substance see Vol. II, p. 74; oxalic acid (*ibid.*, p. 95) can also be used. The most exact results are obtained potentiometrically or with ferroin indicator. Nevertheless the titration can be made visually without an added indicator, if a suitable blank determination is made to correct for the excess of ceric solution needed to produce a yellow color (p. 123). If no catalyst is used the titration must be carried out at 70°C. In the presence of iodine chloride alone it can be done at room temperature, but with ferroin indicator a 50° temperature is necessary.

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[41] H. H. Willard and P. Young, *J. Am. Chem. Soc.*, **50**, 1322 (1928).

[42] H. H. Willard and P. Young, *J. Am. Chem. Soc.*, **55**, 3260 (1933).

[43] E. H. Swift and C. H. Gregory, *J. Am. Chem. Soc.*, **52**, 901 (1930).

Procedure with Iodine Chloride and Ferroin: Weigh out enough sodium oxalate to reduce about 30 ml. of the ceric sulfate solution (0.20 g. for $0.1N$) and place in a 250 ml. beaker with about 75 ml. of water. Add 20 ml. of $12M$ hydrochloric acid and 1.5 ml. of $0.017M$ iodine chloride (p. 132). Heat the solution to 50°C., add 2–3 drops of $0.01M$ ferroin, and titrate with ceric sulfate until the solution becomes pale blue in color and the pink does not return within 1 minute. Do not let the temperature drop below 45° or exceed 50°C. while titrating.

Note: Wheatley[44] states that the titration using ferroin as indicator can be done at room temperature when manganous sulfate is used as catalyst. He adds 25 ml. of 10 per cent manganous sulfate solution, 2.5 ml. of $18N$ sulfuric acid, and 3 drops of $0.025M$ ferroin to 25 ml. of $0.01N$ sodium oxalate solution and then titrates with ceric sulfate solution (4–5 g. of ceric sulfate and 30 ml. of concentrated sulfuric acid diluted to 1 liter with water). After the first addition the solution turns blue, but the red color returns and the titration can then be continued rapidly to the blue end-point.

Watson[45] also recommends this catalyst for the direct titration of oxalate, but prefers to heat to 40–50°C. One milliliter of a $0.01M$ solution and 1 drop of $0.025M$ ferroin are used.

Procedure with Iodine Chloride Alone: Dissolve the weighed sodium oxalate in 100 ml. of water, add 25 ml. of $12M$ hydrochloric acid plus 1.5 ml. of $0.017M$ iodine chloride, and titrate at room temperature. During titration the solution is pure yellow. Near the end-point it becomes darker with free iodine, and the last additions of oxidant convert the iodine to iodine chloride so that the yellow color gradually disappears.

Note: Methylene blue[46] can be used as an indicator in the preceding method. Two drops of 0.1 per cent solution are added 0.2–0.3 ml. before the end-point. The color of the solution changes from yellow through green to bluish pink and finally to blue on standing. The procedure no longer has practical importance.

Procedure without a Catalyst: Place the required quantity of sodium oxalate, accurately weighed, in a beaker and dissolve in 200 ml. of water plus 10–20 ml. of concentrated hydrochloric acid. Warm to 70°C. and titrate with the ceric solution to a permanent, faint yellow. Prepare a blank with the same quantities of water and acid, add 1 ml. of concentrated sulfuric acid, and titrate to the same end-point (about 0.04–0.05 ml. of $0.1N$ solution).

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[44] V. R. Wheatley, *Analyst*, 69, 207 (1944).

[45] J. P. Watson, *Analyst*, 76, 177 (1951).

[46] F. S. Sinnatt, *Analyst*, 35, 309 (1910); 37, 252 (1912).

Notes: (1) Phosphoric and hydrofluoric acids react with cerium(IV) and prevent appearance of the yellow color. Nitric acid causes interference with the oxidation if as much as 5 ml. is present.

(2) Swift and Gregory[43] worked with solutions containing 5 ml. of H_2SO_4 as the only acid. They corrected for the excess ceric ion by saturating the solution with carbon dioxide while cooling, then adding potassium iodide and titrating the liberated iodine with 0.01*N* thiosulfate.

Procedure Using Back-Titration with Mohr's Salt:[39] Dissolve the sodium oxalate, accurately weighed, in a mixture of 150–200 ml. of *M* sulfuric acid and 50 ml. of ceric sulfate solution. Heat to 40–50 °C. for 5 minutes and allow to cool to room temperature. Add ferroin indicator and titrate the excess of ceric sulfate with a solution of Mohr's salt which has previously been evaluated against the ceric sulfate using the same indicator.

Smith and Getz[47] found that sodium oxalate or oxalic acid in 2*N* perchloric acid solution can be titrated at room temperature with ceric perchlorate or nitrate, but not with ceric sulfate. Nitroferroin (p. 127) serves as indicator and is preferable to ferroin for this application because of its higher oxidation potential. More recently, Smith[35] has described the standardization of nitrate-free ceric perchlorate solutions (p. 129).

Procedure: Transfer a weighed sample of sodium oxalate (0.2–0.3 g. for a 0.1*N* solution of ceric perchlorate) to a 400 ml. beaker. Dissolve in 150 ml. of *M* perchloric acid. Titrate the solution until the end-point is near, add 1 drop of 0.025*M* nitroferroin, and continue the titration until the pink color disappears.

Notes: (1) The reaction proceeds at room temperature.

(2) The indicator precipitates as the ferrous perchlorate complex when first added, but dissolves after a few seconds stirring. Electromagnetic stirring is recommended.

(3) There is little warning of the approach of the end-point and the use of a "titration thief" (p. 30) is suggested.

Standardization of 0.001N Ceric Perchlorate Solution: Saloman, Gabrio, and Smith[48] standardized very dilute ceric nitrate or perchlorate solutions against 0.001*N* sodium oxalate in the presence of enough perchloric acid to make its concentration 2*M* at the end-point. For a volume of 10 ml., 0.5 ml. of 0.00025*M* nitroferroin indicator (p. 127) is used. The color change is from pink to colorless and there is a blank correction of about 0.1 ml. of 0.001*N* ceric solution.

Note that sodium oxalate solutions are relatively unstable.

(*c*) ***Standardization against Ferrous Iron:*** Mohr's salt (p. 56) has been used as a standard substance and erioglaucine A as indicator by Furman and Wallace.[3]

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[47] G. F. Smith and C. A. Getz, *Ind. Eng. Chem., Anal. Ed.*, 10, 304 (1938).

[48] K. Saloman, B. W. Gabrio, and G. F. Smith, *Arch. Biochem.*, 11, 436 (1946).

Procedure. Pipette 25 ml. of the ceric solution to be tested into a beaker and add 20 ml. of water and 5–10 ml. of $6N$ sulfuric acid. Titrate with freshly prepared $0.1N$ ferrous ammonium sulfate solution until the cerium is nearly all reduced, then add 0.5 ml. of 0.1 per cent erioglaucine indicator (p. 25) and continue the titration, with thorough stirring, to a permanent change from red to yellow or yellow-green.

Notes: (1) Of course, the iron solution can be titrated with ceric sulfate using ferroin as indicator. Since it is difficult to make pure Mohr's salt or test its purity, it may be better to prepare the ferrous iron solution from metallic iron which is now commercially available in the pure state.

(2) The titration is not very satisfactory for standardizing ceric perchlorate[49] when ferroin is used as indicator. The end-point is satisfactory with 2-2′-dipyridyl (p. 126) if excess of ferrous sulfate is added and back-titrated with ceric sulfate; the solution should be $1N$ in hydrochloric acid. This is unexpected in view of the lower potential of dipyridyl [Authors].

Standardization against Ferrous Ethylenediamine Sulfate: Ceric solutions may also be standardized against ferrous ethylenediamine sulfate (cf. p. 58). Unfortunately, there are insufficient critical studies available as yet concerning this substance, but the method involving its use appears to be the simplest of the many methods of standardization which have been described.

(*d*) ***Standardization against Potassium Ferrocyanide:*** For the purification and drying of potassium ferrocyanide see p. 53. Claassen and Visser[50] used this material for standardizing ceric sulfate. The titration was carried out in $2N$ sulfuric acid solution with ferroin as indicator. Titers obtained averaged 0.08 per cent higher than against carbonyl iron or arsenic trioxide. In hydrochloric acid solution the values were 0.3 per cent low. The advantages of potassium ferrocyanide are its high equivalent weight and convenience of manipulation; further tests are needed before it can be recommended for work of the highest accuracy.

(*e*) ***Standardization against Potassium Iodide:*** Potassium iodide has been recommended as a standard substance for ceric sulfate and permanganate by Kolthoff, Laitinen, and Lingane.[51] The titrations are made in the presence of acetone. Good results are obtained when $0.1N$ solutions are used, but not with $0.01N$ solutions; the results are then low by 0.8–1 per cent owing to reduction of the oxidizing agent by acetone and iodoacetone in the vicinity of the end-point.

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[49] T. Rigg, *Analyst*, 79, 307 (1954).

[50] A. Claassen and J. Visser, *Rec. trav. chim.*, 60, 213 (1941); cf. K. Someya, *Z. anorg. u. allgem. Chem.*, 181, 183 (1929); 184, 428 (1929), as well as N. H. Furman and O. M. Evans, *J. Am. Chem. Soc.*, 51, 1128 (1929), who employed potentiometric methods.

[51] I. M. Kolthoff, H. A. Laitinen, and J. J. Lingane, *J. Am. Chem. Soc.*, 59, 429 (1937); I. M. Kolthoff and H. A. Laitinen, *ibid.*, 61, 1690 (1939).

Procedure: Dissolve 0.35 g. of potassium iodide in 75 ml. of water, add 5 ml. of 18*N* sulfuric acid, 3 drops of 0.025*N* ferroin indicator, and 20–25 ml. of C.P. acetone. Mix and titrate until the color change from red to practically colorless persists for 30 seconds.

3. Methods for Inorganic Compounds. ***Antimony:*** Willard and Young[52] showed that trivalent antimony in hydrochloric acid solution can be titrated with ceric sulfate. Fifteen milliliters of concentrated acid should be present per 100 ml. of solution, along with 5 ml. of 0.005*M* iodine chloride. One drop of 0.025*M* ferroin indicator is introduced at the beginning and the solution is kept at 50°C. during titration. If the acidity is too low some antimony hydrolyzes; if too high, the color does not change at the end-point.

Přibil[53] reported difficulties with this titration which he ascribed to the formation of an antimony(V) complex with *o*-phenanthroline. Satisfactory results were obtained when methyl orange was used as indicator with or without the addition of iodine monochloride. Lang and Fürstenau[54] used osmic acid as catalyst (p. 131) and found that in the presence of tartaric acid high results were obtained. They recommend that the titration be done in sulfuric or hydrochloric acid solutions in the presence of iodine cyanide. The same procedure may be used to titrate arsenic(III).

Hammock, Brown, and Swift[55] attempted to titrate antimony to an iodine monochloride end-point in the presence of carbon tetrachloride (see p. 74). They found the titration to be difficult and tedious even at the optimum acidity of 2.5–3*M*, and concluded that iodate and permanganate are preferable to ceric sulfate for this purpose.

Arsenic: Trivalent arsenic is oxidized smoothly by tetravalent cerium in the presence of either iodine chloride or osmium tetroxide as a catalyst. Both procedures are discussed in connection with the standardization of ceric solutions (p. 131).

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[52] H. H. Willard and P. Young, *J. Am. Chem. Soc.*, **55**, 3268 (1933); cf. H. Rathsburg, *Ber.*, **61**, 1664 (1928).

[53] R. Přibil, *Chem. Listy*, **39**, 19 (1945).

[54] R. Lang and I. Fürstenau, *Z. anal. Chem.*, **133**, 72 (1951).

[55] E. W. Hammock, R. A. Brown, and E. H. Swift, *Anal. Chem.*, **20**, 1048 (1948).

Lang[56] reported that a trace of potassium ferricyanide makes osmium tetroxide ineffective; iodide or iodate, on the other hand, acts as a catalyst even in the presence of ferricyanide. To titrate a mixture of ferrocyanide and arsenite with ceric sulfate, Lang first determined the former by titrating without a catalyst, with ferroin as indicator. In the presence of chromic salts (as in the analysis of zinc green), the color change is from brownish to bright green. At the end-point a drop of $0.01M$ potassium iodate and 1–2 g. of sodium chloride are added, whereupon the color reverts to brown. The titration is continued until the arsenite is oxidized, as shown by a final change to green.

If an osmium catalyst is used, the reverse titration of ceric solution with arsenite does not go so well as the direct titration. It is advisable to treat the oxidant with an excess of arsenite and back-titrate with ceric reagent.

In hydrochloric acid medium even the direct titration is not suitable when osmium tetroxide is employed as catalyst and ferroin as indicator. The first drop of reagent oxidizes the indicator and the red color returns but slowly even when arsenite is present in considerable excess. However, small amounts of chloride do not interfere seriously in sulfuric acid solution, such as a mixture $1N$ in sulfuric acid and $0.1N$ in hydrochloric, though the color change is less sharp. By adding an excess of mercuric perchlorate one can bind the chloride ions and avoid interference.

Smith and Fritz[57] showed that micro quantities of trivalent arsenic in $2N$ perchloric acid can be titrated with $0.001N$ ceric perchlorate in the same acid, using 5-nitro-1,10-phenanthroline (nitroferroin) as indicator. For the standardization of $0.001N$ reagent against sodium oxalate see p. 134. In titrations of 0.15–0.26 mg. of arsenic trioxide, the maximum error was 4.2 and the average error 1.2μg.

Cerimetric Determination of Traces of Arsenic: Kolthoff and Amdur[58] convert arsenate or arsenite to elemental arsenic by reduction with hypophosphite reagent.[59,60] After filtration the arsenic is oxidized to the pentavalent state with excess ceric sulfate and the excess is determined with standard arsenite.

Reagents: Calcium hypophosphite solution. Dissolve 200 g. of calcium hypophosphite in $6N$ hydrochloric acid and dilute with this acid to 1 liter.

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[56] R. Lang, *Z. anal. Chem.*, **115**, 103 (1938). Lang credits W. Böhm with having observed the effect first.

[57] G. F. Smith and J. S. Fritz, *Anal. Chem.*, **20**, 874 (1948).

[58] I. M. Kolthoff and E. Amdur, *Ind. Eng. Chem., Anal. Ed.*, **12**, 177 (1940).

[59] R. Engel, *Compt. rend.*, **96**, 498 (1883); J. Thiele, *Apoth. Ztg.*, **5**, 86 (1890); R. Engel and J. Bernard, *Compt. rend.*, **122**, 390 (1896).

[60] L. Brandt, *Chem. Ztg.*, **37**, 1445, 1471, 1496 (1913); **38**, 295, 461, 474, 984 (1914); B. S. Evans, *Analyst*, **54**, 523 (1929); **57**, 492 (1932).

Standard arsenite solution, 0.005N. Prepare by dilution of stock 0.05N arsenic trioxide solution, p. 43.

Standard ceric sulfate solution, 0.005N. Prepare by diluting a stock 0.05N solution, p. 129, with N sulfuric acid. Allow to stand for 1 week before standardizing, or standardize along with each determination.

Indicator solution. A saturated solution of ferrous phenanthroline perchlorate in water.

Catalyst solution. Osmium tetroxide, 0.05 g. in 20 ml. of 0.1N sulfuric acid.

Procedure: Prepare the sample so that not more than 2.0 mg. of arsenic is present in 25 ml. of solution (in a 250 ml. Erlenmeyer flask). Add 10 ml. of hypophosphite solution and 35 ml. of concentrated hydrochloric acid. Heat the mixture for 10 minutes at 80–90°C. (on a hot plate) but do not allow it to boil. After no further darkening is observed, bring to a gentle boil and keep boiling for 5 minutes to coagulate the arsenic. Remove from the hot plate, allow to cool slightly, and filter on a small asbestos filter or micro filter tube. Rinse the flask and filter 3 or 4 times with water. Transfer the pad and precipitate to the original flask. Measure in a 25–50 per cent excess of 0.005N ceric sulfate and swirl to break up the precipitate. Heat the solution to 40–50 for 2–3 minutes and swirl the contents as they cool, until no dark spots of arsenic remain.

Cool and add 0.1 ml. of osmium catalyst and 2 ml. of indicator for every 50 ml. of ceric sulfate introduced. Titrate with 0.005N arsenite to the first appearance of a reddish color or, better, add excess arsenite and titrate back with ceric solution to the disappearance of the red color. Determine the indicator correction by running a blank. One milliliter of 0.005N ceric solution is equivalent to 0.075 mg. of arsenic.

Notes: (1) Results are generally accurate to within 5μg. when the quantity of arsenic is between 0.1 and 2.0 mg.

(2) Mercury interferes, but lead, tin, antimony, copper, and iron do not. According to Evans,[60] chromium, tin, and antimony interfere in his procedure for hypophosphite reduction, in which the acidity is lower. Tungsten produces a blue color. He gives methods to be used in their presence.

(3) Selenium and tellurium compounds interfere since they are also reduced to the elemental state by hypophosphite. Challis[61] precipitates them first by heating the hypophosphite–3N hydrochloric acid mixture at 50°C. for half an hour. The precipitate is removed, after which arsenic is reduced by heating to higher temperature.

(4) The precipitated arsenic can also be determined iodometrically according to Evans,[60] or with bromate-bromide solution (p. 512).

Application of the Arsenite Titration: *Chlorate*: Gleu[62] studied the catalytic influence of osmium tetroxide on reduction of chlorate by arsenious acid.

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[61] H. J. G. Challis, *Analyst*, 66, 58 (1941).

[62] K. Gleu, *Z. anal. Chem.*, 95, 385 (1933).

In a mixture of 10 ml. of 0.1N chlorate, 15 ml. of 0.1N arsenious acid, 3 drops of 0.01M osmic acid, and 100 ml. of N sulfuric acid, the reduction of chlorate is quantitative after 1 hour standing at room temperature. It is very interesting that the reaction between arsenious acid and ceric sulfate (in presence of osmic acid) induces the reduction of chlorate by arsenious acid so strongly that the excess of arsenious acid can be immediately titrated with ceric sulfate at room temperature, using ferroin as indicator. Although arsenite can be titrated with ceric sulfate in the presence of osmic acid without interference from air, induced air-oxidation does occur when arsenite is oxidized simultaneously by chlorate and cerium(IV). Thus, when the excess of arsenious acid is titrated, the air must be removed by the addition of bicarbonate. Surprisingly, osmic acid does not catalyze the reduction of persulfate by arsenious acid; also the reaction between ceric sulfate and arsenious acid has no inducing effect. Thus chlorate can be determined in presence of persulfate by the following method.

Procedure: To reduce the chlorate solution in 100–150 ml. of N sulfuric acid add excess of 0.1N arsenious acid; remove air by careful addition of sodium bicarbonate (2–3 g.). After adding 3 drops of 0.01M osmic acid and 2 drops of 0.01M ferroin, titrate the solution dropwise with 0.1N ceric sulfate from red to colorless.

Notes: (1) As a control that the excess of arsenious acid has been enough (20 per cent suffices), add 5 ml. of 0.1N arsenious acid to the titrated solution, which must consume exactly 5 ml. of 0.1N ceric sulfate in the back-titration. In this way, the results obtained are about 0.2 per cent high owing to air interference. When large amounts of chloride are present, at least as much M mercuric perchlorate solution as will bind all the chloride as mercuric chloride is added before the removal of air.

(2) Permanganate can be used for the back-titration; the induced reaction effect and the air interference are less than with ceric sulfate, but a larger excess of arsenious acid is required for quantitative reduction of chloric acid.

Nitrogen Compounds. *Azide:* Hydrazoic acid is oxidized quantitatively to nitrogen by an excess of ceric ammonium nitrate:[63]

$$2N_3^- + 2Ce^{4+} \longrightarrow 3N_2 + 2Ce^{3+}$$

Arnold[64] gives the following method for assaying lead or sodium azide.

Procedure: Place 0.3 g. of the azide, accurately weighed, in a 250 ml. Erlenmeyer flask containing 50 ml. of water (100 ml. in the case of sodium azide). From a burette add 50 ml., or a definite excess, of 0.1N ceric ammonium nitrate solution containing 64 ml. of concentrated nitric acid per liter. Gently agitate, wash down the sides of the flask with water, and introduce a drop of 0.025M ferroin indicator. Titrate back with 0.1N ferrous sulfate in

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[63] F. Sommer and H. Pincas, *Ber.*, **48**, 1965 (1915); J. Martin, *J. Am. Chem. Soc.*, **49**, 2133 (1927).

[64] J. W. Arnold, *Ind. Eng. Chem., Anal. Ed.*, **17**, 215 (1945).

6*N* sulfuric acid. Shortly before the end-point add enough 1:1 sulfuric acid to make its concentration 1*M* in the final solution. The end-point is a change from pale green to reddish yellow.

Note: Heavy metal azides are violently explosive; for precautions and further details see the original paper.

Hydroxylamine: Benrath and Ruland[65] stated that nitrous oxide and nitrogen were produced by the oxidation of hydroxylamine sulfate with ceric sulfate. The reaction is too slow for direct titration but a back-titration method is described by Cooper and Morris,[66] who found that the reaction was in accord with the equation:

$$2NH_2OH + 4Ce(SO_4)_2 \longrightarrow N_2O + 2Ce_2(SO_4)_3 + H_2O + 2H_2SO_4$$

Procedure: Place 50 ml. of 0.1*N* ceric sulfate solution in *N* sulfuric acid in a 500 ml. Erlenmeyer flask. Add 15 ml. of 6*N* sulfuric acid and bring to gentle boiling. While boiling, add 25 ml. of hydroxylamine sulfate or hydrochloride solution. Boil gently for 1 minute, cool, and dilute to 150 ml. Add 2 drops of 0.01*M* osmium tetroxide catalyst and back-titrate with 0.1*N* arsenious acid solution; add 2 drops of ferroin indicator near the endpoint.

Note: The results obtained for the hydrochloride salt were slightly higher than those for the sulfate, presumably because of a slight oxidation of the chloride ion. It might be better to add excess arsenite and back-titrate (cf. p. 137).

Nitrite: A procedure for the determination of nitrite, in which a known quantity of ceric sulfate is titrated with the unknown nitrite solution, was published in 1905 by Barbieri.[67] Willard and Young[68] demonstrated that the titration is quantitative if the ceric sulfate solution, containing 5–10 ml. of nitric acid per 100–200 ml., is warmed to 50–60°C. The tip of the burette containing the nitrite solution should dip just below the surface of the liquid. Ferroin indicator should not be added until nearly all the ceric ion has been reduced, and the titration from this point should be completed very slowly.

Bennett and Harwood[69] applied the method to the determination of potassium as potassium cobaltinitrite. The precipitate is dissolved in an excess of ceric sulfate solution which is back-titrated with ferrous ammonium sulfate using ferroin indicator or iodometrically. An empirical factor is necessary to relate the net titration volume to the potassium content of the precipitate.

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[65] A. Benrath and K. Ruland, *Z. anorg. Chem.*, **114**, 267 (1920).

[66] S. R. Cooper and J. B. Morris, *Anal. Chem.*, **24**, 1360 (1952).

[67] G. Barbieri, *Chem. Ztg.*, **29**, 668 (1905).

[68] H. H. Willard and P. Young, *J. Am. Chem. Soc.*, **55**, 3260 (1933); **51**, 139 (1929); **50**, 1379 (1928); cf. Atanasiu.[4]

[69] A. H. Bennett and H. F. Harwood, *Analyst*, **60**, 677 (1935); cf. D. S. Brown, R. R. Robinson, and G. M. Browning, *Ind. Eng. Chem., Anal. Ed.*, **10**, 652 (1938); O. J. Kelley, A. S. Hunter, and A. J. Sterges, *ibid.*, **18**, 319 (1946); I. A. Kaye, *ibid.*, **12**, 310 (1940); H. C. Harris, *Soil Sci.*, **40**, 301 (1935).

Stubblefield[70] determines nitrogen dioxide (or nitrous acid in the presence of nitric acid) by reaction with strongly acid 0.1N ceric ammonium nitrate and back-titration with oxalate.

$$NO_2 + Ce^{4+} + H_2O \longrightarrow NO_3^- + Ce^{3+} + 2H^+$$

$$NO_2^- + 2Ce^{4+} + H_2O \longrightarrow NO_3^- + 2Ce^{3+} + 2H^+$$

The ceric reagent is prepared from ceric ammonium nitrate with perchloric acid as described on p. 129, but with 170 ml. of 72 per cent acid per liter. It is standardized against sodium oxalate, using nitroferroin as indicator. The method is claimed to be more rapid and to have fewer disadvantages than the permanganate method (p. 69).

Procedure: Place 5 ml. of 72 per cent perchloric acid and 100 ml. of water in a 250 ml. beaker. To this add 25–50 ml. of 0.1N ceric reagent, accurately measured, depending upon the quantity of nitrous acid expected. Pipette a 10 ml. sample into the solution, with the tip of the pipette well below the surface at the beginning but raised until it barely touches the surface at the end. Allow the mixture to stand for 1–2 minutes, then stir slowly. Add 2–3 drops of nitroferroin (p. 127) and titrate with 0.1N sodium oxalate solution.

Phosphorus Compounds: By suitable adjustment of the temperature, hypophosphite and phosphite can be oxidized selectively with ceric sulfate. Bernhart[71] has described methods based on this principle for the determination of hypophosphite in the presence of phosphite and of total hypophosphite and phosphite. Hypophosphite is oxidized quantitatively to phosphite in 2 hours at room temperature or in 30 minutes at 60°C. Phosphite is unaffected. Phosphite and hypophosphite are oxidized quantitatively to phosphate at 80–100°C.

$$2Ce^{4+} + H_3PO_2 + 2H_2O \longrightarrow H_3PO_4 + 4Ce^{3+} + 4H^+$$

$$2Ce^{4+} + H_3PO_3 + H_2O \longrightarrow H_3PO_4 + 2Ce^{3+} + 2H^+$$

Procedure. (*a*) *Hypophosphite:* To about 0.1 g. of sodium hypophosphite add 25 ml. of 1:4 sulfuric acid and 50 ml. of 0.1N ceric sulfate solution. Stir and set aside for at least 2 hours at room temperature or heat for 30 minutes at 60°C. Cool, add 1 drop of 0.025M ferroin indicator and back-titrate with a 0.1N solution of Mohr's salt.

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[70] F. M. Stubblefield, *Ind. Eng. Chem., Anal. Ed.*, **16**, 366 (1944); cf. G. Barbieri, *Chem. Ztg.*, **29**, 668 (1905).

[71] D. N. Bernhart, *Anal. Chem.*, **26**, 1798 (1954); cf. M. N. Sastri and C. Kalidas, *Rec. trav. chim.*, **74**, 1045 (1955).

(*b*) *Hypophosphite and Phosphite:* Proceed as above but add 50 ml. of 1:4 sulfuric acid and boil for 15 minutes. Cool and titrate.

Notes: (1) Rao and Rao[72] claim that Bernhart's method yields irregular results. They recommend boiling the solution in the presence of silver catalyst, which accelerates the reaction and enables lower concentrations of sulfuric acid and ceric sulfate to be used. Both hypophosphite and phosphite are oxidized with excess of ceric sulfate at boiling water-bath temperatures during 30 minutes in $2N$ sulfuric acid with 5 ml. of 2 per cent silver sulfate catalyst. It is not possible to differentiate between the two compounds by this procedure.

(2) Sodium hypophosphate was determined by Moeller and Quinty[73] by oxidizing with an excess of ceric solution in the presence of nitric acid and back-titrating with a standard arsenite solution, using osmic acid catalyst and potentiometric detection of the end-point. The method is not applicable when phosphite and hypophosphite are present.

(3) Deshmukh[74] determines red phosphorus by oxidizing with an excess of ceric sulfate and back-titrating with a standard ferrous solution. White phosphorus is oxidized only superficially.

Thiosulfate: The determination of thiosulfate by ceric sulfate was studied by Furman and Wallace.[75]

They recommended that potassium iodide be added to the thiosulfate solution before the titration. Starch is used as indicator. The iodine color appears transiently during the course of the titration but it reacts rapidly with the thiosulfate.

Procedure: To about 0.6 g. of hydrated sodium thiosulfate dissolved in water add 0.3–0.4 g. of potassium iodide and 20 ml. of 0.2 per cent starch solution. Dilute to about 250 ml. with water. Titrate with ceric sulfate to a permanent starch-iodine color, taking care to mix the solution thoroughly during the course of the titration.

Note: Lang and Kurtenacker[76] determined thiosulfate by oxidizing with ferric sulfate in the presence of copper as catalyst and then titrating the ferrous ion formed with ceric sulfate. By suitable modification the method can be operated in the presence of sulfites. Dithionates and polythionic acids do not interfere.

Iodide: Willard and Young[77] demonstrated potentiometrically that iodide can be titrated with ceric sulfate according to the equation:

$$2Ce^{4+} + 2I^- \longrightarrow 2Ce^{3+} + I_2$$

The end-point cannot be located visually in this system, but by application of Lang's cyanide procedure (p. 46) or a modified Berg method (p. 47) it is possible to obtain good results. Lewis[78] made use of ferroin as indicator in a Berg titration:

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[72] K. B. Rao and G. G. Rao, *Z. anal. Chem.*, **147**, 274, 279 (1955).

[73] T. Moeller and G. H. Quinty, *Anal. Chem.*, 24, 1354 (1952).

[74] G. S. Deshmukh, *Analyst*, **76**, 604 (1951).

[75] N. H. Furman and J. H. Wallace, *J. Am. Chem. Soc.*, **53**, 1283 (1931).

[76] R. Lang and H. Kurtenacker, *Z. anal. Chem.*, **123**, 169 (1942).

[77] H. H. Willard and P. Young, *J. Am. Chem. Soc.*, **50**, 1368 (1928).

$$2Ce^{4+} + I^- + C_3H_6O \longrightarrow 2Ce^{3+} + C_3H_5OI + H^+$$

Procedure: Treat 10–20 ml. of about 0.1*M* iodide solution in an Erlenmeyer flask with 25 ml. of acetone, 10 ml. of 1:1 sulfuric acid, 1 drop of 0.025*M* ferroin solution, and water to make about 100 ml. Titrate the solution with 0.1*M* ceric ammonium sulfate solution to the change from pink to pale blue. The end-point is sharp and remains for several minutes. If free iodine is formed at the beginning, it disappears quickly upon stirring.

Notes: (1) The titration of 10 ml. of 0.1*M* iodide in the presence of an equivalent quantity of bromide gives a good result; but in the presence of more bromide the results become too high unless a corresponding dilution is made. Bromide-iodide ratios as great as 5:1 can be titrated at sufficient dilution, with errors not exceeding 0.4 per cent. In diluting the halides, the concentrations of acetone and acid should be kept roughly constant.

(2) Slightly high results are found if much chloride is present, but 0.5 g. of sodium chloride causes no error.

Hydrogen Peroxide: The reaction of hydrogen peroxide with ceric sulfate

$$2Ce^{4+} + H_2O_2 \longrightarrow 2Ce^{3+} + 2H^+ + O_2$$

was shown to be quantitative in potentiometric titrations by Atanasiu[4] and by Furman and Wallace.[3] Willard and Young[79] obtained good results by titrating at 20–25°C. in the presence of 5–30 ml. of hydrochloric acid per 100–200 ml. of solution, with ferroin as indicator. The method is stated to work well even in the presence of organic matter.[80]

In the analysis of mixtures containing Caro's acid (H_2SO_5) and peroxydisulfuric acid ($H_2S_2O_8$), Berry[81] determines hydrogen peroxide cerimetrically at 0°C. without interference from the other compounds. About 1 ml. less than the required volume of ceric sulfate is placed in a flask and cooled by addition of ice, then the sample is measured in and the titration is completed. Berry did not use an indicator other than the yellow color of tetravalent cerium. Caro's acid can be determined in the same solution by reduction with excess vanadyl sulfate and titration of the excess with permanganate. The sum of H_2SO_5 and $H_2S_2O_8$ can be found by reduction with excess ferrous sulfate, which can then be back-titrated with permanganate (p. 80) or dichromate (p. 177).

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[78] D. Lewis, *Ind. Eng. Chem., Anal. Ed.*, 8, 199 (1936).

[79] H. H. Willard and P. Young, *J. Am. Chem. Soc.*, 55, 3260 (1933); cf. E. C. Hurdis and H. Romeyn, *Anal. Chem.*, 26, 320 (1954).

[80] J. S. Reichert, S. A. McNeight, and H. W. Rudel, *Ind. Eng. Chem., Anal. Ed.*, 11, 195 (1939).

[81] A. J Berry, *Analyst*, 58, 464 (1933).

Csányi and Solymosi[82] analyzed similar mixtures by reduction with standard arsenite solution (different conditions being required for the three constituents) and back-titration with ceric sulfate. The original work should be consulted for details.

Perborate reacts with ceric sulfate in the same way as hydrogen peroxide.

Greenspan and MacKellar[83] determined hydrogen peroxide in the presence of aliphatic per acids (peroxy acids) and diacyl peroxides by titrating with 0.1*N* ceric sulfate in 150 ml. of 5 per cent sulfuric acid at 0–10°C. Ferroin serves as the indicator. The titration solution is then used for iodometric determination of the per acids at the same temperature. Diacyl peroxides do not react rapidly enough to interfere in either titration under these conditions. Cerium(IV) is to be preferred to permanganatebeca use there is less interference from organic compounds.

Mercury: Mercurous salts are not easily oxidized to mercury(II) by oxidizing titrants. According to Willard and Young,[84] the oxidation is quantitative if a 50–100 per cent excess of ceric sulfate is used in a solution of volume 200 ml. containing 10–50 ml. of sulfuric acid (sp. gr. 1.5) and if the mixture is heated for 30–60 minutes at just below the boiling point. When more than 30–35 mg. of mercurous ion is determined, a blank test with an approximately equal amount of mercuric salt should be run. Considerable amounts of mercuric ion cause some decomposition of ceric solutions.

Reifer[85] determined 0.1–2 mg. of mercury(II) by treating a solution of mercuric chloride with an excess of standard iodide solution. The reactions are as follows:

$$Hg^{2+} + 4I^- \longrightarrow HgI_4{}^{2-}$$

$$HgI_4{}^{2-} + 2Ce^{4+} \longrightarrow HgI_2 + I_2 + 2Ce^{3+}$$

Any iodide used in excess of that necessary for the formation of the complex $HgI_4{}^{2-}$ is also oxidized to iodine by ceric sulfate solution. The method can be operated in the presence of phosphates and chlorides.

Thallium: Willard and Young[86] found that the following conditions bring about complete oxidation of monovalent to trivalent thallium.

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[82] L. J. Csányi and F. Solymosi, *Z. anal. Chem.*, **142,** 143 (1954).

[83] F. P. Greenspan and D. G. MacKellar, *Anal. Chem.*, **20,** 1061 (1948).

[84] H. H. Willard and P. Young, *J. Am. Chem. Soc.*, **52,** 557 (1930).

[85] I. Reifer, *Roczniki Chem.*, **26,** 340 (1952).

[86] H. H. Willard and P. Young, *J. Am. Chem. Soc.*, **52,** 36 (1930).

The sample is brought to a volume of about 200 ml., acidified with 20 ml. of hydrochloric acid and 3–5 ml. of sulfuric acid (both concentrated), and titrated at 80–90 °C. with 0.1*N* ceric sulfate to persistence of a faint yellow color. A correction of 0.05 ml. is applied for the required excess of reagent.

Notes: (1) The presence of sulfuric acid or sulfate is necessary to prevent a partial reduction of tetravalent cerium by hydrochloric acid. Nitric acid interferes even in small quantities.

(2) Berry[87] titrated with iodine chloride as indicator, in the presence of much hydrochloric acid (see p. 461). Swift and Garner[88] state that this method is unsatisfactory because of the sluggish nature of the reaction.

Rhenium: Rhenium in its tri- or tetravalent state can be oxidized under suitable conditions to perrhenate, Re(VII). Geilmann and Wrigge[89] found that rhenium oxide was rapidly oxidized by gentle heating with ceric sulfate, but that rhenium trichloride required boiling for 5–10 minutes and potassium chlororhenate, K_2ReCl_6, for 15–20 minutes.

Procedure: Add the solid 0.05–0.15 g. sample to 25 ml. of 0.1*N* ceric sulfate and warm or boil to obtain complete oxidation. Cool and back-titrate with standard ferrous sulfate, using ferroin indicator.

Tellurium: In warm acid solution ceric sulfate oxidizes tellurous acid, but the reaction does not readily go to completion. Willard and Young[90] found that a chromic salt can serve as a catalyst. Tetravalent cerium oxidizes chromium(III) to chromium(VI), which in turn oxidizes tellurous ions to telluric (cf. p. 192).

Procedure: To the sample solution add 10 ml. of 1:1 sulfuric acid, 10–20 mg. of chromium in the form of a chromic salt, and water to make 200 ml. Add a measured quantity of standard ceric sulfate in excess and boil for 5–10 minutes. Titrate the excess oxidant with a reducing solution such as ferrous sulfate.

Note: Selenious acid and cupric salts do not interfere if the acidity is not too great.

Tin: Stannous tin in hydrochloric acid solution can be titrated with ceric sulfate solution.[91] The use of potassium iodide plus starch as the indicator eliminates the interference of iron and certain other elements, making the titration quite similar to the usual iodometric method (p. 319). The presence of a little antimony is beneficial; oxygen must be excluded. The method can be applied after reduction of stannic tin by the method of Hallett[92] in which nickel is used.

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[87] A. J. Berry, *Analyst*, **54**, 461 (1929).

[88] E. H. Swift and C. S. Garner, *J. Am. Chem. Soc.*, **58**, 113 (1936).

[89] W. Geilmann and F. W. Wrigge, *Z. anorg. u. allgem. Chem.*, **222**, 56 (1935).

[90] H. H. Willard and P. Young, *J. Am. Chem. Soc.*, **52**, 553 (1930).

[91] L. G. Bassett and L. F. Stumpf, *Ind. Eng. Chem., Anal. Ed.*, **6**, 477 (1934).

Lykken and Tuemmler[93] titrated stannous and ferrous ions in 3*N* hydrochloric acid successively with ceric sulfate, using a platinum indicator electrode and glass reference electrode. It may be possible to find redox indicators for this system, since the end-point potentials are well separated. Differential reduction, with nickel, of iron in cold solution and of iron plus tin in hot solution is also possible (p. 22). Ferroin should be a suitable indicator for titration of the reduced solutions with ceric sulfate.

Suzuki[94] noted that antimony(III) and arsenic(III) interfered in the titration, but their effect could be overcome by the addition of sodium pyrophosphate and arsenic(V), respectively. He recommends that the solution of tin(II) be added to an excess of ceric sulfate to avoid atmospheric oxidation.

Chromium and Vanadium: Chromium can be determined by oxidation with excess of ceric sulfate in hot solution followed by back-titration with sodium oxalate or nitrite solution. Alternatively, the excess can be decomposed and chromic acid titrated with standard ferrous sulfate. Vanadium is determined similarly; the titrations are done potentiometrically.[95] Chromium(III) has also been determined by oxidation to chromium(VI) with ammonium persulfate in the usual way; an excess of standard ferrous solution is then added and back-titrated with ceric sulfate solution. Large amounts of vanadium interfere but may be separated first by precipitation with cupferron at pH 1.2–1.6.[96]

Potentiometric titration of vanadium(IV) with ceric sulfate is quantitative in sulfuric, hydrochloric, or perchloric acid solution at 70–75°C.[97] or at 50–60°C.[98] Vanadyl perchlorate has been titrated potentiometrically in 8*N* perchloric acid solution with standard ceric nitrate in perchloric acid.[99] No visual end-point methods appear to have been described for the determination of this metal.

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[92] R. L. Hallett, *J. Soc. Chem. Ind.*, **35**, 1087 (1916).

[93] L. Lykken and F. D. Tuemmler, *Ind. Eng. Chem., Anal. Ed.*, 14, 68 (1942).

[94] S. Suzuki, *J. Chem. Soc. Japan*, **73**, 89, 115 (1952).

[95] H. H. Willard and P. Young, *J. Am. Chem. Soc.*, **51**, 139 (1929); *Trans. Electrochem. Soc.*, 67, 347 (1935).

[96] *Analytical Chemistry of the Manhattan Project*, C. J. Rodden, ed., McGraw-Hill, New York, 1950, p. 445.

[97] H. H. Willard and P. Young, *Ind. Eng. Chem.*, 20, 972 (1928).

[98] N. H. Furman, *J. Am. Chem. Soc.*, **50**, 755 (1928).

[99] G. F. Smith and C. A. Getz, *Ind. Eng. Chem., Anal. Ed.*, **10**, **191** (1938).

Ferrous Iron: Ferrous iron is usually titrated in sulfuric acid medium, but the presence of hydrochloric acid can be tolerated. The titration may be carried out at acidities between $0.5M$ and $3M$ in either hydrochloric or sulfuric acid. Reverse titration is possible and may be preferable in some cases; $0.01N$ reagents can be used if an indicator correction is applied. The titration was first used by Willard and Young[100] but became of greater practical importance when Walden, Hammett, and Chapman[101] introduced ferrous 1,10-phenanthroline as indicator.

Procedure: Prepare the sample solution to contain 0.15–0.20 g. of ferrous iron in 150 ml. of M sulfuric acid. Add 1 drop of $0.025M$ ferroin indicator (p. 127) and titrate with $0.1N$ ceric sulfate to the change from pink to nearly colorless.

Notes: (1) Thiry[102] studied the effect of various substances on the determination of ferrous iron with ceric sulfate, particularly for the analysis of pharmaceutical products. Iodides must be removed with a silver salt. Oxalic acid and citric acid interfere but benzoic acid, most saturated aliphatic acids, and succinic acid do not. Salicylic and gallic acids produce interfering colors. Acacia gum, tragacanth, methanol, ethanol, glycerol, sucrose, and lactose may be present.

(2) The use of 2,2′-dipyridyl ferrous perchlorate complex as indicator for the ferrous iron titration has been recommended by Cagle and Smith[25] (see p. 126). Under the conditions given in the procedure above, 1 ml. of saturated aqueous indicator solution is taken and the indicator correction is about 0.02 ml. of $0.1N$ ceric reagent. The end-point is a change from orange to colorless in the direct titration; in the presence of hydrochloric acid the final solution is colored yellow from ferric chloride complexes. The change is quite reversible since a slight excess of oxidant does not destroy the indicator rapidly.

(3) Suzuki[103] and Lang and Fürstenau[54] have described methods by which iron, arsenic, antimony, and tin may be determined when present together. For the titration of small amounts of iron in presence of antimony, arsenic, and tin(II), the paper by Petzold[104] should be consulted. Fluoride interferes in the titration but can be masked by the addition of boric acid.[105]

Application of the Ferrous Titration: *Persulfate:* Persulfate is reduced by ferrous salts and may be determined by back-titration of the excess with ceric sulfate. Organic compounds interfere strongly; they are oxidized by persulfate owing to an induced reaction promoted by that between persulfate and ferrous iron. Bromide suppresses this induced oxidation.[106] Kolthoff and Carr[107] applied the method in the presence of ethanol, methanol, allyl acetate, allyl alcohol, and methyl isopropenyl ketone and used sodium bromide to inhibit the induced reactions.

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[100] H. H. Willard and P. Young, *J. Am. Chem. Soc.*, **50**, 1334 (1928).

[101] G. H. Walden, L. P. Hammett, and R. P. Chapman, *J. Am. Chem. Soc.*, **53**, 3908 (1931); **55**, 2649 (1933).

[102] G. Thiry, *J. Pharm. Belg.*, **2**, 121 (1947).

[103] S. Suzuki, *J. Chem. Soc. Japan*, **74**, 429, 529 (1953); **73**, 200 (1952).

[104] A. Petzold, *Z. anal. Chem.*, **149**, 258 (1956).

[105] Cf. I. Lange and A. Petzold, *Z. anal. Chem.*, **150**, 24 (1956).

Procedure: To 10 ml. of 0.005–0.025N persulfate solution in a 125 ml. Erlenmeyer flask add water, 7 ml. of 5N sodium bromide (Note 1), and 2 ml. of 6N sulfuric acid. Swirl and add excess of 0.05N ferrous sulfate in 0.5N sulfuric acid (5 ml.). Stopper, swirl, and set aside for 20 minutes; the total volume should be 35 ml. Add 2 ml. of 0.0005M ferroin and titrate the excess of ferrous sulfate with 0.02N ceric sulfate in a solution of N sulfuric acid (Note 2).

Notes: (1) The optimum concentration of bromide is 1N. Lower concentrations do not quantitatively inhibit the induced oxidation, and higher concentrations affect the sharpness of the end-point.

(2) The indicator changes from red to very pale blue at the end-point, but the solution is yellow and therefore the change is orange to yellow. In the presence of N bromide the orange color returns in 30 seconds. The first color change which is sharp and accurate should be taken. The indicator blank is negligible.

(3) For 20–30 mg. samples the error is ±0.5 per cent; for 6 mg. samples, ±2 per cent.

Ferrocyanide (cf. p. 135): Willard and Young[52] titrated ferrocyanide at room temperature in 100–200 ml. of solution containing 5–10 ml. of hydrochloric acid, with ceric sulfate as reagent and ferroin as indicator. Claassen and Visser[50] claimed that somewhat better results are obtained in 2N sulfuric acid. Sinn[108] used 5–10 ml. of 5N acid, either hydrochloric or sulfuric, per 100 ml., but he added an alkali bromide to the solution.

Notes: (1) The titration was studied potentiometrically by Furman and Evans[109] before ferroin came into use. When the ceric solution was made up to contain 4 mg. of ferric iron per 100 ml. they could also recognize the end-point visually, the color changing from a ferric ferrocyanide blue-green during the titration to nearly colorless at the end. Berry[110] used diphenylamine as indicator.

(2) Burriel, Lucena, and Bolle[111] recommended ceric sulfate for the titration of ferrocyanide in the presence of cyanide. The method was satisfactory with solutions containing 5 ml. of hydrochloric or 6 ml. of sulfuric acid per 100 ml.

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[106] I. M. Kolthoff, A. I. Medalia, and H. P. Raaen, *J. Am. Chem. Soc.*, **73**, 1733 (1951).

[107] I. M. Kolthoff and E. M. Carr, *Anal. Chem.*, **25**, 298 (1953).

[108] V. Sinn, *Ann. chim. anal.*, **28**, 166 (1946); *Chem. Abstr.*, **41**, 53 (1947).

[109] N. H. Furman and O. M. Evans, *J. Am. Chem. Soc.*, **51**, 1128 (1929); cf. J. A. Atanasiu and V. Stefanescu, *Ber.*, **61**, 1343 (1928); K. Someya, *Z. anorg. u. allgem. Chem.*, **181**, 183 (1929).

[110] A. J. Berry, *Analyst*, **54**, 461 (1929).

[111] F. M. Burriel, F. C. Lucena, and S. Bolle, *Anal. Chim. Acta*, **7**, 302 (1952).

Applications of the Ferrocyanide Titration. *Hydrazine:* In alkaline medium, hydrazine is quantitatively oxidized by ferricyanide[112] according to the equation:

$$N_2H_4 + 4K_3Fe(CN)_6 + 4KOH \longrightarrow N_2 + 4K_4Fe(CN)_6 + 4H_2O$$

Dernbach and Mehlig[113] determined hydrazine from the amount of ferrocyanide which is formed.

Procedure: To a sample containing about 0.1 g. of hydrazine sulfate in 25–35 ml. of water in a 250 ml. Erlenmeyer flask add 10 ml. of $0.5M$ potassium ferricyanide and 10 ml. of $6N$ sodium hydroxide. Shake gently for 30 seconds, set aside for at least 2 minutes, and add 30 ml. of $6N$ hydrochloric acid and enough water to give a total volume of 100 ml. Titrate with $0.1N$ ceric sulfate until the green color fades to a permanent brownish color.

Notes: (1) For a sharper change, 2–3 drops of $0.5M$ ferric chloride can be added within 4–5 ml. of the end-point. The amount of ferricyanide must be adjusted carefully; too little causes incomplete reaction, and too much creates difficulties with the end-point. Ferroin could probably be used as indicator (see below).

(2) Results are accurate to about 0.1 per cent in the absence of interfering substances. Hydroxylamine is oxidized to nitrogen and nitrous oxide under the conditions employed.[112]

Hydroxylamine: Sant[114] has described a method similar to that given for hydrazine. In a buffered solution at pH 9–10, hydroxylamine is oxidized to nitrogen by ferricyanide and the ferrocyanide formed is titrated with ceric sulfate.

Procedure: Add a two- to three-fold excess of standard potassium ferricyanide solution to the sample of hydroxylamine (as hydrochloride). Add 25–50 ml. of buffer solution (8 g. of borax and 4 g. of boric acid per 100 ml. of water). Shake the vessel occasionally over a period of 20 minutes, acidify with 1:1 hydrochloric acid or 1:5 sulfuric acid, and titrate the ferrocyanide produced with ceric sulfate solution, using ferroin or ferric chloride as indicator.

Note: The excess of ferricyanide is critical (cf. Hydrazine, Note 1, above).

Other Applications: Suseela determines thiocyanate[115] and vanadium(IV)[116] by oxidation with alkaline ferricyanide and titration of the ferrocyanide formed. Zinc in magnesium alloys can be determined by adding excess of standard ferrocyanide and back-titrating, after some time, with ceric sulfate.[117] Calcium can be precipitated as ferrocyanide from ethanolic solution and titrated after dissolution in sulfuric acid.[118] Ferricyanide can be titrated with ceric sulfate using cacotheline or indigo carmine as indicator after reduction with liquid tin amalgam.[119] The original papers should be consulted for details of these determinations.

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[112] P. R. Ray and H. K. Sen, *Z. anorg. Chem.*, **76**, 380 (1912).

[113] C. J. Dernbach and J. P. Mehlig, *Ind. Eng. Chem., Anal. Ed.*, **14**, 58 (1942).

[114] B. R. Sant, *Z. anal. Chem.*, **145**, 257 (1955).

[115] B. Suseela, *Z. anal. Chem.*, **145**, 175 (1955).

[116] *Idem., Anal. Chim. Acta*, **13**, 543 (1955).

Determination of Metal Compounds after Reduction. ***Ferric Iron:*** Ferric iron can be reduced to ferrous in a number of ways, some of which have been mentioned on p. 83. One of the methods most suitable for reduction before titration with ceric sulfate involves the use of the silver reductor, as proposed by Walden, Hammett, and Edmonds.[120] For a description of the reductor see p. 14.

Procedure: Prepare the ferric solution to contain 0.1–0.2 g. of iron in 50 ml. of M hydrochloric acid. Pass this through the reductor at a rate of about 30 ml. per minute, catching in a 600 ml. beaker. Rinse the column with 150 ml. of M hydrochloric acid. If vanadium is present, add 200 ml. of $10M$ sulfuric acid to the beaker and cool the mixture thoroughly. Add 1 drop of $0.025M$ ferroin indicator and titrate with $0.1N$ ceric sulfate.

Notes: (1) When vanadium is present, the solution titrated should be $5M$ in sulfuric acid. Under these conditions the indicator changes after all the ferrous iron has been oxidized, the vanadium remaining in the tetravalent state to which it was reduced in the column. Titanium, chromium, and manganese do not interfere, and up to 0.2 g. of nitric acid may be tolerated, either in the M hydrochloric acid or the $5M$ sulfuric acid solution. Molybdenum must be absent; it may be removed by double precipitation of the ferric iron with ammonium hydroxide.

(2) Moderately small amounts of iron (10–20 mg.) may be reduced and titrated with $0.01N$ ceric sulfate in the same way, if an indicator correction, which amounts to 0.2–0.3 ml., is determined and subtracted. For micro determinations it is necessary to consider the interfering action of hydrogen peroxide which is formed when air is present in the silver reductor (see p. 15). Edmonds and Birnbaum[121] minimize the interference by using a reductor which is scaled down in proportion to the amount of iron expected. For 0.6–2.7 mg. of iron in 10 ml. of N hydrochloric acid, they recommend a reductor 20 cm. long and 1 cm. in diameter. The column is washed with 20 ml. of N acid and the solution, containing 2 drops of $0.001M$ ferroin, is titrated with $0.01N$ ceric sulfate from a 5 ml. microburette. The indicator correction is about 0.01 ml. Errors of -0.003 to $+0.006$ mg. are reported.

For the determination of 0.03–0.6 mg. of ferric iron in silicate rocks, Miller and Chalmers[122] recommend washing the reductor with N hydrochloric acid saturated with carbon dioxide. The variable peroxide error is thus eliminated without excluding air. Gold crucibles are used instead of platinum for sample fusion because platinum(IV) is reduced to platinum(II) in the reductor and is only slowly oxidized by ceric ion. Collection of the effluent and titration are carried out in an atmosphere of carbon dioxide.

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[117] L. G. Miller, A. J. Boyle, and R. B. Neill, *Ind. Eng. Chem., Anal. Ed.*, **16**, 256 (1944).

[118] H. Flaschka and H. Spitzy, *Mikrochemie*, **35**, 306 (1950).

[119] C. Yoshimura, *J. Chem. Soc. Japan*, **74**, 704 (1953).

[120] G. H. Walden, Jr., L. P. Hammett, and S. M. Edmonds, *J. Am. Chem. Soc.*, **56**, 350 (1934).

[121] S. M. Edmonds and N. Birnbaum, *Ind. Eng. Chem., Anal. Ed.*, **12**, 60 (1940).

[122] C. C. Miller and R. A. Chalmers, *Analyst*, **77**, 2 (1952).

(3) Lang and Fürstenau[123] reduce with thiosulfate (with or without a copper catalyst) and decompose the excess with selenious acid. The advantage claimed over the usual reductants is that interferences are less.

Flaschka[124] prefers to use liquid zinc amalgam for the reduction of 1–6 mg. amounts of iron. For the analysis of ferric saccharate, Huizinga[125] dissolves 1 g. of sample in 25 ml. of dilute sulfuric acid, adds 1 g. of iron-free zinc, and heats for 1 hour on the water bath. The solution is cooled, filtered, and titrated with ceric sulfate, using ferroin as indicator. Ferric albuminate and organic ferrous preparations may be analyzed likewise.

Sastri and Murti[126] recommend sodium hypophosphite as a reducing agent. The titration with ceric sulfate is made in the presence of excess of the reductant.

Procedure: To the solution of ferric iron add an excess of 5 per cent sodium hypophosphite and sufficient hydrochloric acid to give a final concentration of 2–3M. Boil for 15–20 minutes, cool under the tap, and titrate with ceric sulfate using N-phenylanthranilic acid as indicator.

Notes: (1) Sulfuric acid cannot be used since the reaction is too slow in this medium. At hydrochloric acid concentrations above and below 2–3M the reduction is incomplete.

(2) Potassium permanganate cannot be used because it oxidizes the excess hypophosphite. Potassium dichromate also reacts with hypophosphite in the presence of ferrous iron. An induced reaction is caused by the primary fast reaction between dichromate and iron(II).

Potassium ferrate may be determined by reducing with an excess of arsenite and titrating with ceric sulfate solution in the usual way, or by reducing first with stannous chloride and titrating the ferrous iron formed.[127]

Copper: Birnbaum and Edmonds[128] reduce copper(II) to the cuprous state with a silver reductor (p. 14). The solution during passage through the reductor should be 2N in hydrochloric acid, although up to 3 g. of nitric acid per 50 ml. may also be present without causing trouble. The effluent is collected under 0.5M ferric ammonium sulfate solution prepared by dissolving the salt in 0.5M sulfuric acid. One drop of 0.025M ferroin indicator is added and the ferrous iron equivalent to the cuprous copper is titrated with 0.1N ceric sulfate.

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[123] R. Lang and I. Fürstenau, *Z. anal. Chem.*, **133**, 163, 331 (1951).

[124] H. Flaschka, *Mikrochemie*, **35**, 36 (1950).

[125] T. Huizinga, *Pharm. Weekblad*, 85, 723 (1950).

[126] M. N. Sastri and C. R. K. Murty, *Z. anal. Chem.*, **147**, 16 (1955).

[127] J. M. Schreyer, G. W. Thompson, and L. T. Ockerman, *Anal. Chem.*, **22**, 691 (1950).

[128] N. Birnbaum and S. M. Edmonds, *Ind. Eng. Chem., Anal. Ed.*, **12**, 156 (1940).

Note: Iron, uranium, molybdenum, and vanadium must be absent. Iron may be removed by double precipitation with ammonia in the presence of ammonium chloride. No interference was encountered in titration of a reduced copper solution containing 0.05 g. of pentavalent arsenic and 0.1 g. each of zinc, stannic tin, bismuth, and cadmium. Copper alone may be determined with an accuracy of about 1 part per thousand.

Cuprous Chloride: The following procedure is recommended for the assay of cuprous chloride by Hatch and Estes.[129] With an appropriate decrease in the quantity of ferric iron taken, the procedure may be applied to dilute cuprous solutions.

Procedure: Prepare a ferric ammonium sulfate solution by dissolving 10 g. of the crystals in enough 3M sulfuric acid to make 100 ml. Weigh 0.3 g. of the sample to be tested into a dry Erlenmeyer flask and add 25 ml. of the ferric solution. Swirl until all is dissolved, add a drop of ferroin indicator, and titrate with 0.1N ceric sulfate. Run a blank on the reagents and subtract from the titration.

Metallic Copper: Baker and Gibbs[130] developed procedures for the analysis of cuprous–cupric oxide mixtures which contain metallic copper.

The cuprous oxide is dissolved in 100 ml. of an extraction solution containing 40 ml. of hydrochloric acid and 40 g. of fresh stannous chloride dihydrate per liter of ethanol. Any cupric oxide that dissolves is reduced to cuprous by the tin chloride without the metal being attacked. During this operation, the temperature is kept near 0°C. with lumps of dry ice. After filtration and washing with ethanol, the residue of copper and cupric oxide is dissolved by warming with 25 ml of a solution containing 75 g. of ferric chloride hexahydrate, 150 ml. of hydrochloric acid, and 400 ml. of water. The ferrous iron produced is titrated with 0.1N ceric sulfate after the addition of 50 ml. of water and 3 drops of ferroin indicator. The change is from orange to pale green.

Total reducing power (copper plus cuprous oxide) can be determined by digesting a portion of the original sample directly with 10 ml. of ferric chloride–hydrochloric acid solution for 15 minutes in a carbon dioxide atmosphere. The titration is carried out as before. Cupric oxide is not measured in either procedure, but may be calculated after a determination of total copper.

Note: After electrolytic separation of the metal, Bradford and Kirk[131] determined micro quantities of copper (0.5–1 mg.) by placing the washed gauze electrode in 10 ml. of standard $0.01N$ ceric sulfate which is $0.5N$ in chloride. The chloride must be added to increase the rate of dissolution of the copper. After a few minutes of stirring of the electrode, the excess of ceric sulfate is back-titrated with standard ferrous solution, ferroin being used as indicator.

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[129] L. F. Hatch and R. R. Estes, *Ind. Eng. Chem., Anal. Ed.*, **18**, 136 (1946).

[130] I. Baker and R. S. Gibbs, *Ind. Eng. Chem., Anal. Ed.*, **18**, 124 (1946); **15**, 505 (1943).

[131] L. H. Bradford and P. L. Kirk, *Ind. Eng. Chem., Anal. Ed.*, **13**, 64 (1941).

Molybdenum: Either metallic mercury or silver reduces hexavalent molybdenum to the pentavalent state quantitatively in $2–3.5N$ hydrochloric acid. More powerful reductants, e.g., amalgamated zinc, take the reduction to the trivalent state. In this form the reduced molybdenum is very unstable and is allowed to flow directly into a ferric solution; the ferrous iron so formed is then titrated. Furman and Murray[132] have shown that the reduced solutions in the pentavalent state are stable for several hours in contact with air and can be titrated accurately with standard ceric sulfate.

Procedure with Mercury: Place 25 ml. of mercury in a bottle or flask, pipette in a molybdate solution containing 0.2–0.3 g. of molybdic oxide, and add enough hydrochloric acid to make the acidity about $3N$. Shake vigorously by hand or with a machine for 5 minutes, then decant the solution through a filter into a 600 ml. beaker. Wash the mercury and mercurous chloride five times with 20 ml. portions of 1:5 hydrochloric acid, shaking well for a few seconds each time, and decanting through the filter. Reserve the reductor for subsequent determinations.

To the filtrate, add 10–20 ml. of 1:1 sulfuric acid and enough 1:5 hydrochloric acid to make the total volume 300 ml. Add 2 drops of $0.025M$ ferroin indicator and titrate with $0.1N$ ceric sulfate.

Notes: (1) If the acid normality is less than 1.5 during the reduction, molybdenum blue may precipitate. Above $4N$, some trivalent molybdenum is likely to be produced; this effect becomes quantitative in $9N$ hydrochloric acid if oxygen is excluded.

(2) Phosphate and arsenate in amounts up to 0.25 g. do not interfere. Up to 5 g. of ammonium chloride or sulfate may be present. Even traces of copper interfere seriously by causing catalytic oxidation of pentavalent molybdenum:[133]

$$Cu^{2+} + Mo^{5+} \longrightarrow Cu^{+} + Mo^{6+}$$

$$2Cu^{+} + 2H^{+} + O_2 \longrightarrow H_2O_2 + 2Cu^{2+}$$

$$2Mo^{5+} + 2H^{+} + H_2O_2 \longrightarrow 2Mo^{6+} + 2H_2O$$

$$(4Mo^{5+} + 4H^{+} + O_2 \xrightarrow{Cu^{2+}} 4Mo^{6+} + 2H_2O) \quad \text{(overall)}$$

Procedure with Silver:[134] To 50 ml. of solution, approximately $0.1M$ in molybdenum and $2M$ in hydrochloric acid, add 3 ml. of 85 per cent phosphoric acid. Heat to 60–80°C. Pretreat the silver reductor with hot $2M$ hydrochloric acid at a rate of about 10 ml. per minute, then pass the molybdate solution through and collect it in a 400 ml. beaker. Wash the column with 150 ml. of $2M$ hydrochloric acid, using hot acid for the first few washings and allowing the last 100 ml. to pass through at a higher rate. Cool the reduced solution, add a drop of $0.025M$ ferroin, and titrate with $0.1M$ ceric sulfate. The last 0.3–0.4 ml. should be added dropwise with vigorous stirring, for a precipitate of ceric phosphate forms and redissolves rather slowly. Run a blank on the reagents, mainly to compensate for iron present in the acids.

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[132] N. H. Furman and W. M. Murray, *J. Am. Chem. Soc.*, **58**, 1689 (1936).

[133] W. M. Murray and N. H. Furman, *J. Am. Chem. Soc.*, **58**, 1843 (1936).

[134] N. Birnbaum and G. H. Walden, *J. Am. Chem. Soc.*, **60**, 64 (1938); cf. C. F. Hiskey, V. F. Springer, and V. W. Meloche, *ibid.*, **61**, 3125 (1939).

Notes: (1) As in the other reduction-oxidation methods for molybdenum, elements such as iron, copper, and vanadium would interfere. Nitrate also interferes, its reduction being catalyzed by the presence of molybdate. As little as 0.2 mg. interferes with the sharpness of the end-point; with larger quantities, nitrogen oxides are formed in the reductor and the results for molybdenum are low.

(2) Birnbaum and Walden[135] applied the method to the determination of phosphorus as ammonium molybdiphosphate. Silicate must be absent, for otherwise a variable ratio of molybdate to phosphate is obtained. The precipitation of the ammonium molybdiphosphate must also be made in the absence of nitrates or nitric acid; ammonium chloride and hydrochloric acid are used and the precipitate is washed with acidified ammonium sulfate solution. It is redissolved in $2M$ sodium hydroxide, then the solution is treated with hydrochloric acid and phosphoric acid, and passed through the reductor.

Determination of Thorium as Thorium Molybdate: In about 7 per cent acetic acid solution, thorium can be precipitated[136] as the normal molybdate, $Th(MoO_4)_2$. Banks and Diehl[137] determine thorium in this way but pass the dissolved precipitate through a Jones reductor and titrate the trivalent molybdenum (cf. p. 153).

Procedure: Dilute the sample of thorium, preferably as the nitrate and in an amount equivalent to 0.15–0.2 g. of thorium oxide, to 150 ml. in a nearly neutral aqueous solution. Add 11 ml. of glacial acetic acid, 15 ml. of thick filter paper pulp, and 1 ml. of alcoholic diphenylcarbazide solution (0.25 per cent). Introduce ammonium paramolybdate solution (7.6 g. per liter) from a burette, with stirring, until the indicator turns deep pink. Allow to settle and test for complete precipitation, adding more reagent if required. Heat to boiling and filter while hot through a retentive 11 cm. paper into a 400 ml. beaker. Wash 5–6 times with hot 1:100 acetic acid.

Return the filter and precipitate to the original beaker and add 25 ml. of concentrated hydrochloric acid. Stir until the filter is disintegrated, then add 75 ml. of water. Heat to boiling and filter again in the same way washing with hot 1:100 hydrochloric acid. Cool the filtrate to room temperature and pass through a Jones reductor (p. 13) into a five-fold excess of 10 per cent ferric alum solution containing 2–3 ml. of 85 per cent phosphoric acid. Titrate with 0.1*N* ceric sulfate, using 2 drops of 0.025*M* ferroin as indicator. The end-point is at the change from pink to colorless or light blue.

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[135] N. Birnbaum and G. H. Walden, *J. Am. Chem. Soc.*, 60, 66 (1938).

[136] F. J. Metzger and F. W. Zons, *Ind. Eng. Chem.*, 4, 493 (1912); H. T. S. Britton and W. L. German, *J. Chem. Soc.*, 1931, 1429.

[137] C. V. Banks and H. Diehl, *Anal. Chem.*, 19, 222 (1947).

Notes: (1) The interference of calcium is negligible when the amount of calcium is no greater than that of thorium. With 0.5 g. or more, a double precipitation should be made. Rare earth elements interfere. Up to 0.2 g. of uranium(VI) causes no more than a small positive error if 5 g. of ammonium acetate is added. In this case a larger excess of molybdate (4–6 ml.) should be used; diphenylcarbazide is not satisfactory for revealing the correct amount.

(2) The precipitation method can also be reversed to give a separation of molybdenum from hexavalent uranium and other elements. Banks and Diehl[137] have worked out procedures for the analysis of uranium-molybdenum and thorium-uranium alloys.[138]

Plutonium: Small amounts of plutonium sulfate can be determined by reducing to plutonium(III) in a small Jones reductor and then titrating to the quadrivalent state with 0.0045*N* ceric sulfate solution with ferroin as indicator.[139]

Titanium: Excellent results were obtained by Claassen and Visser[140] in bringing titanium to the trivalent state in a cadmium reductor (p. 17) and titrating with ceric sulfate. The titration can be made directly if air is completely excluded, but it is easier to collect the reduced titanium under a ferric iron solution and to titrate the ferrous iron produced. Ferrous phenanthroline is used as indicator. Various metals interfere (cadmium is a less selective reducing agent than silver, which does not reduce titanium).

Syrokomskii and Silaeva[141] state that the complexes formed by titanium(III) with acetic acid or ammonium sulfate in acid solution are sufficiently stable to overcome interference by atmospheric oxygen during the titration.[142] [The authors doubt this and consider it advisable to maintain a carbon dioxide atmosphere.] The solution is treated with 15 ml. of saturated ammonium sulfate or 10 ml. of acetic acid, passed through a cadmium reductor, and titrated with ceric sulfate solution. Cacotheline indicator (p. 622) is added near the end-point.

Tungsten: Apparently the literature through 1955 does not give methods for the determination of tungsten cerimetrically. Probably the reduced form could be titrated under conditions similar to those which permit titration with permanganate (p. 92).

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[138] Cf. E. R. Wright and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, 9, 251 (1937) and ref. 96, p. 453.

[139] C. W. Koch, NNES., Div. IV, 14B, Transuranium Elements, Pt. II, 1337, 1949.

[140] A. Claassen and J. Visser, *Rec. trav. chim.*, 60, 213 (1941).

[141] V. S. Syrokomskii and E. V. Silaeva, *Zavodskaya Lab.*, 15, 1015 (1949); see also *Z. anal. Chem.*, 132, 120 (1951).

[142] Cf P. Wehber and H. Hahn, *Z. anal. Chem.*, 136, 325 (1952).

Columbium: A method has been described[143] in which columbium(V) is reduced to columbium(III) by electrolytic reduction. The columbium(III) is reacted with ferric solution and the ferrous iron so produced is titrated with ceric sulfate in the presence of ferroin as indicator. The original paper should be consulted for details.

Uranium: The reduction of uranium salts and titration of the products with ceric sulfate were first studied potentiometrically.[144] Passage of a hot or cool uranyl sulfate solution through a Jones reductor yields a mixture of tri- and tetravalent uranium. The trivalent form is rapidly oxidized by air but the tetravalent is fairly stable (up to 4 hours) in air at room temperatures.[145] Birnbaum and Edmonds[146] demonstrated that uranyl sulfate solutions $4M$ in hydrochloric acid yield tetravalent uranium quantitatively on passage through a silver reductor at 60–90°C. A reduced solution can be titrated at 50°C., ferroin being used as indicator, when the only acid present is sulfuric,[147] but better results in hydrochloric acid were obtained in a cool solution to which some phosphoric acid was added.[146]

Procedure of Birnbaum and Edmonds: Dissolve the uranium salt, containing 0.1–0.4 g. of uranium, in 50 ml. of $4M$ hydrochloric acid and heat to 60–90°C. Pretreat a silver reductor (p. 15) with hot $4M$ hydrochloric acid and pass the uranium solution through at a rate of 20 ml. per minute. Wash with 150 ml. of hot acid of the same concentration at a faster rate for the last 100 ml. Cool the reduced solution and add 3 ml. of 85 per cent phosphoric acid and 1 drop of $0.025M$ ferroin indicator. Titrate with $0.1N$ ceric sulfate to disappearance of the pink color. A little silver chloride may precipitate but it does not disturb the determination. A blank should be run and subtracted.

Notes: (1) Interference is caused by iron, copper, molybdenum, vanadium, and possibly other reducible elements. Nitric acid must be absent, but acetic acid causes no trouble.

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[143] O. Tomíček, K. Spurny, L. Jerman, and V. Holeček, *Collection Czech Chem. Communs.*, **18**, 757 (1953).

[144] D. J. Ewing and M. Wilson, *J. Am. Chem. Soc.*, **53**, 2105 (1931); N. H. Furman and I. C. Schoonover, *ibid.*, **53**, 2561 (1931).

[145] G. E. F. Lundell and H. B. Knowles, *J. Am. Chem. Soc.*, **47**, 2637 (1925).

[146] N. Birnbaum and S. M. Edmonds, *Ind. Eng. Chem.*, *Anal. Ed.*, **12**, 155 (1940).

[147] H. H. Willard and P. Young, *J. Am. Chem. Soc.*, **55**, 3260 (1933).

(2) Sutton[148] reduced uranyl salts electrolytically, later oxidizing to the tetravalent form with air. Holmes and Kirk[149] made use of cadmium amalgam as a reducing agent and applied the method to the indirect determination of sodium as the zinc uranyl acetate.[150] The use of a zinc wire spiral for reducing uranium in a hot solution containing 10 ml. of hydrochloric acid per 250 ml. was recommended by McClure and Banks.[151] The spiral is left in the solution during cooling and removed before air is passed through.

(3) Determination of less than 5 mg. of uranium is difficult because of overreduction and failure to attain the desired tetravalent state on reoxidation.[152] Poor results were obtained even with a micro silver reductor which was found to give very incomplete reduction at 50°C. and overreduction at 80°C. However, Pepkowitz[152] has described a successful method involving the use of zinc amalgam in an oxygen-free titration cup. In the titration, 0.02N ceric sulfate was used.

(4) Uranium can be separated from various interfering substances by extraction of the nitrate with ether from a solution saturated with ammonium nitrate.[153] After evaporation of the ether, the nitrate must be eliminated before reduction. Careful fuming with sulfuric acid has been suggested.

(5) Good end-points are also obtained by titrating after the addition of excess ferric alum.[154]

In more recent investigations there appears to be a preference shown for the lead reductor.[155,156] Fritz *et al.*[156] follow the reduction described on p. 190 but titrate with 0.01N ceric sulfate solution; ferroin is used as indicator. Sill and Peterson[155] found that, for the determination of small amounts of uranium in ores, the reductor blank due to hydrogen peroxide formation should be zero.

Procedure:[155] Pass the air-free solution of volume 80 ml. containing 20 ml. of concentrated hydrochloric acid through an air-free lead reductor (p. 16) at a rate of 100 ml. per minute at 25°C. Wash with 80 ml. of N hydrochloric acid. Add 1 ml. of 0.001M ferroin and 1 drop of 85 per cent phosphoric acid, and titrate rapidly with 0.01N ceric sulfate until the color lightens. Add 2 ml. of 85 per cent phosphoric acid and titrate slowly to the end-point.

Note: Large amounts of uranium can be determined similarly if stronger titrant and indicator solutions are used. Two milliliters of 20 per cent ferric alum in 5 per cent sulfuric acid is substituted for the phosphoric acid which is added near the end-point.

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[148] J. Sutton, *Chem. Abstr.*, 42, 6701 (1948).

[149] B. Holmes and P. L. Kirk, *J. Biol. Chem.*, 116, 377 (1936).

[150] Cf. N. H. Furman, E. R. Caley and I. C. Schoonover, *J. Am. Chem. Soc.*, **54**, 1344 (1932).

[151] J. H. McClure and C. V. Banks, MDDC-1044, U. S. Atomic Energy Comm., June 17, 1947; *Proc. Iowa Acad. Sci.*, 55, 263 (1948).

[152] D. A. MacInnes and L. G. Longsworth, MDDC-910, U. S. Atomic Energy Comm., March 4, 1947; L. P. Pepkowitz, MDDC-727, U. S. Atomic Energy Comm., Jan. 28, 1947.

[153] F. Hecht and A. Grunwald, *Mikrochem. ver. Mikrochim. Acta*, **30**, 279 (1942), E. Kroupa, *ibid.*, **32**, 245 (1944).

[154] Ref. 96, p. 67.

[155] C. W. Sill and H. E. Peterson, *Anal. Chem.*, **24**, 1175 (1952).

[156] J. S. Fritz, M. O. Fulda, S. L. Margerum, and E. I. Lane, *Anal. Chim. Acta*, **10**, 513 (1954).

4. Methods for Organic Compounds. ***Oxalic Acid and Oxalates:*** The titration of oxalate solutions has been described in connection with the standardization of ceric solutions (p. 132). An interesting study of the oxidation of oxalic acid with ceric ammonium sulfate in a nonaqueous medium has been made recently.[157] The acetic acid used as the medium participates in the reaction and detection of the end-point by visual and potentiometric methods is unsatisfactory. The titrant is not stable in an acetic acid medium and needs standardizing daily. It is evident that much further investigation will be necessary before it can be decided if the method has any practical applications.

Calcium is frequently determined indirectly after precipitation as calcium oxalate by titrating the precipitate after dissolution in acid with ceric sulfate or perchlorate. The titration procedure is exactly the same as that used for oxalic acid. Many different procedures have been described, particularly in the biochemical journals; it is only possible to refer to a selection here.

Willard and Young[41,42] first used the ceric sulfate method for determining calcium as oxalate. They applied the titrations described on p. 133.

Smith[158] has described a method for the determination of calcium in Iceland spar and dolomite in which precipitation is made from homogeneous solution and the precipitate is titrated with ceric perchlorate.

Procedure: Transfer the sample (100–200 mg.) to a 400 ml. beaker, dissolve in 25 ml. of 1:5 hydrochloric acid, dilute to 200 ml. with water, heat to boiling, and add 0.6 g. of ammonium oxalate. Add 5 g. of urea dissolved in 25 ml. of water and digest at 80–90 °C. for several hours. Test that the solution is basic to methyl orange indicator. Cool and filter through a sintered-glass crucible. Wash several times with small portions of water.

Dissolve the precipitate in hot 5 per cent perchloric acid, cool, and add sufficient perchloric acid to give a final concentration of 1*M*. Titrate with 0.1*N* ceric perchlorate or ceric ammonium nitrate in *M* perchloric acid, using ferroin or nitroferroin as indicator.

Note: Willard and Young's procedure (p. 133) was also applied and gave satisfactory results.

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[157] O. N. Hinsvark and K. G. Stone, *Anal. Chem.*, **28**, 334 (1956).

[158] Ref. 40, p. 80.

Steigman, Birnbaum, and Edmonds[26] introduced a new indicator, ruthenium tridipyridyl dichloride (p. 126).

Procedure (Oxalate or Oxalic Acid): Add 2 drops of 0.02*M* indicator solution to 100 ml. of 2*M* perchloric acid in which 0.12–0.15 g. of sodium oxalate is dissolved. Titrate at room temperature with 0.1*M* ceric nitrate. The end-point is shown by the color change from yellow to colorless.

For the titration of micro quantities (0.04–1 mg.) of oxalic acid, Kirk and Tompkins[159] add to 1 ml. of the solution sufficient 2*N* sulfuric acid to give a final acidity of 0.5–1*N* after adding all reagents and an excess (twice or three times the theoretical amount) of 0.1*N* ceric sulfate, and heat the mixture for 30 minutes on a steam bath. When cool, the excess of ceric cerium is back-titrated with standard Mohr's salt solution, using ferrous phenanthroline or setopaline C as indicator. The procedure is suitable for the determination of micro quantities of calcium after precipitation as oxalate. Oxalic acid can also be titrated directly at room temperature with ceric perchlorate in about *N* perchloric acid, setopaline C being used as indicator until a final color change from yellow to red is obtained.

Saloman, Gabrio, and Smith[48] applied their microtitration procedure for oxalate (p. 134) to the determination of calcium in blood plasma, after wet-ashing with a perchloric-nitric acid mixture and precipitation as calcium oxalate. Excellent results were obtained over the range 10–120 μg. of calcium.

For other micro methods the original papers should be consulted.[160]

Other Organic Acids: The oxidation of various acids was studied systematically by Willard and Young.[161] Formic and acetic acids, and presumably higher fatty acids also, are quite stable toward ceric sulfate even in hot solution. Succinic acid also escapes oxidation. The following general conditions were found suitable for the determination of the acids listed in Table IV.

Procedure: Treat the appropriate quantity of sample (see Table IV) with sulfuric acid (see Table IV) and an excess of 0.1*N* ceric sulfate. Heat the solution at 90–95°C., the appropriate time depending on the particular com-

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[159] P. L. Kirk and P. C. Tompkins, *Ind. Eng. Chem., Anal. Ed.*, **13**, 277 (1941).

[160] G. H. Ellis, *Ind. Eng. Chem., Anal. Ed.*, **10**, 112 (1938); O. J. Kelley, A. S. Hunter, and A. J. Sterges, *ibid.*, **18**, 319 (1946); C. D. Kochakian and R. P. Fox, *ibid.*, **16**, 762 (1944); E. Katzman and M. Jacobi, *J. Biol. Chem.*, **118**, 539 (1937); C. E. Larson and D. M. Greenberg, *ibid.*, **123**, 199 (1938); R. Lindner and P. L. Kirk, *Mikrochemie*, **22**, 291 (1937); E. Berger, *Clin. Chem.*, **1**, 249 (1955).

[161] H. H. Willard and P. Young, *J. Am. Chem. Soc.*, **52**, 132 (1930); cf. A. Benrath and K. Ruland, *Z. anorg. Chem.*, **117**, 267 (1920); A. J. Berry, *Analyst*, **37**, 461 (1929); C. Fromageot, *J. chim. phys.*, **24**, 513, 623 (1927); C. Cortés Guardia, *Afinidad*, **27**, 289 (1950).

TABLE IV

Acid	Sample wt. (mg.)	H_2SO_4, sp. gr. 1.5 (ml.)	Total volume (ml.)	Heating period at 90–95°C. (min.)	Amt. of 0.1N Ce^{4+} (ml.)	Equivalents per mole
Tartaric	21.3–159.8	15–45	100–300	10–60	30–100	7.2
Malonic	17.3–86.7	20–80	80–400	15–60	35–100	6.66
Malic	33.8–59.3	20–60	200	15–120	50–75	9.25
Glycolic	20.05–102.6	20–60	100–300	30–120	50–75	3.95
Citric	50.0–70.0	20–75	110–300	30–60	60–100	15.85

pound being oxidized. After cooling, back-titrate the remaining oxidant with a standard ferrous solution, using ferroin as indicator.

Note: For the determination of malonic acid, Willard and Young[161] found it necessary to add the ceric sulfate solution before the sulfuric acid because the latter attacks the organic acid.

Fumaric, maleic, and phthalic acid are only very slightly affected under these conditions. Benzoic acid is oxidized only slowly and salicylic acid somewhat more rapidly, but procedures for their determination have been worked out recently.

Sharma and Mehrotra[162] have reexamined the conditions for the oxidation of various organic acids with ceric sulfate and have shown that the reaction can be accelerated by increasing the concentration of sulfuric acid. Under the recommended conditions the final oxidation products are carbon dioxide and water, and the reactions are stoichiometric (see Table V).

TABLE V

Acid	Weight of sample (mg.)	Total time of heating (min.)	Equivalent of oxygen	Sulfuric acid (% concn.)
Formic	4–18	50–90	2.00	66
Tartaric	10–25	65–85	10.00	66
Malonic	10–20	60	8.00	66
Malic	8–17	60	12.00	66
Glycolic	5–13	65–70	6.00	66
Maleic	3–15	60–90	11.98	50
Fumaric	3–15	150–180	11.93	50
Benzoic	2–5	120–150	29.92	66
Phthalic	1–5	180–240	29.88	50
Salicylic	1–4	150–180	28.01	50

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[162] N. N. Sharma and R. C. Mehrotra, *Anal. Chim. Acta*, 11, 417, 507 (1954).

Procedure: Add the acid to a cooled mixture of $0.1N$ ceric sulfate (in $2N$ sulfuric acid) and sufficient sulfuric acid to give a 50 or 66 per cent concentration (see Table V). Heat on a boiling water bath in a flask fitted with a reflux condenser for the appropriate time (see Table V). Cool, dilute to 200 ml. with water, and titrate the excess of ceric sulfate with a $0.1N$ solution of Mohr's salt using *N*-phenylanthranilic acid as indicator.

Notes: (1) Formic, tartaric, malic, and glycolic acids should be mixed with ceric sulfate and heated for 10–15 minutes; sufficient concentrated sulfuric acid is then added through the condenser to give a 66 per cent solution and the solution is heated for a further 50 minutes. The determination is then completed as above. If the concentrated acid is added at first, the oxidation takes longer. With malonic acid, the initial rate of oxidation is not affected by sulfuric acid. Acetic and succinic acids could not be oxidized.

(2) Fromageot and Desnuelle[163] determined pyruvic acid by adding it to a solution of ceric sulfate in N sulfuric acid and back-titrating after 5 minutes with a solution of Mohr's salt. The reaction proceeds:

$$CH_3CO{\cdot}COOH + 2Ce^{4+} + H_2O \qquad CH_3COOH + 2Ce^{3+} + 2H^+ + CO_2$$

(3) Takahashi, Kimoto, and Sakurai[164] have described methods for the determination of various amino acids. Although these acids are fairly stable to ceric sulfate oxidation, their hydroxy derivatives, obtained by reaction with nitrous acid, are readily oxidized:

$$NH_2R{\cdot}COOH + HONO \qquad HO{\cdot}R{\cdot}COOH + N_2 + H_2O$$

The excess of nitrous acid is simply removed by boiling. A sample solution containing 5–60 mg. and 20 ml. of $3N$ sulfuric acid is diluted to 70 ml. with water and treated with 2 ml. of 30 per cent sodium nitrite solution. The solution is heated slowly at first and then more strongly for 15 minutes, 5 ml. of $0.1N$ ceric sulfate is added, and the mixture is refluxed for 15 minutes. The cooled solution is diluted with water to 100 ml. and titrated with a $0.1N$ solution of Mohr's salt. The reactions are not stoichiometric (Table VI).

TABLE VI

Amino acid	Moles of oxygen consumed
Glycine	1.23
Alanine	2.86
Glutamine	4.75
Arginine	3.14
Cystine	9.24

The reproducibility is within 2 per cent; there is no interference from impurities such as thiourea or ammonium sulfate.

Hydroxy Compounds: The principles involved in the oxidation of organic substances with ceric perchlorate in $4N$ perchloric acid have been investigated by Smith and Duke.[165] The following is a summary of their results:

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[163] C. Fromageot and P. Desnuelle, *Biochem. Z.*, **279**, 174 (1935).

[164] T. Takahashi, K. Kimoto, and H. Sakurai, *Repts. Inst. Ind. Science, Univ. Tokyo*, **5**, 121 (1955).

1. In each case an even number of equivalents of oxidant is required. End products are fatty acids, ketones, aldehydes (other than formaldehyde and carbon dioxide). The oxygen uptake is stoichiometric.
2. Only compounds in which protons are removed from oxygen are readily oxidized.
3. The carbonyl group before oxidation must hydrate to the glycol form. Compounds containing an active methylene are oxidizable.
4. Formaldehyde is hydrated and oxidized to formic acid.
5. Oxalic acid is instantly oxidized at ordinary temperatures. The reaction is used in the determination of the excess of ceric cerium with nitroferroin as indicator.

The oxidation reactions of some representative types of organic compounds are given below.

Citric acid:

$$C_6H_8O_7 + 14Ce^{4+} + 5H_2O \longrightarrow 4CO_2 + 2HCOOH + 14H^+ + 14Ce^{3+}$$

Polyhydroxy alcohols:

$$CH_2OH(CHOH)_nCH_2OH - (2n + 6)e + (n + 2)H_2O \longrightarrow (n + 2)HCOOH + (2n + 6)H^+$$

Polyhydroxy alcohol monocarboxylic acids:

$$CH_2OH(CHOH)_nCOOH - (2n + 4)e + (n + 1)H_2O \longrightarrow (n + 1)HCOOH + (2n + 4)H^+ + CO_2$$

Aldoses:

$$CH_2OH(CHOH)_nCOH - (2n + 4)e + (n + 2)H_2O \longrightarrow (n + 2)HCOOH + (2n + 4)H^+$$

Ketoses:

$$CH_2OH(CHOH)_2COCH_2OH - (2n + 8)e + (n + 3)H_2O \longrightarrow (n + 2)HCOOH + (2n + 8)H^+ + CO_2$$

In order to oxidize organic compounds quantitatively and stoichiometrically a time limit of 120 minutes or less has been established. Solutions of ceric perchlorate in 4*N* perchloric acid may be heated at 60°C. for 60 minutes without appreciable loss in titer. Formic and acetic acid are not appreciably oxidized by this solution in the same period of time. With *acetaldehyde* and *acetone* present as products of the reaction of oxidation, more than *5 minutes at 10°C.* causes appreciable error.

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[165] G. F. Smith and F. R. Duke, *Ind. Eng. Chem., Anal. Ed.,* **15**, **120** (**1943**).

In Table VII the conditions are given for quantitative oxidation of various compounds (Smith and Duke).

TABLE VII

Quantitative Oxidation of Hydroxy Compounds with Ceric Perchlorate in 1 *N* Perchloric Acid (Smith and Duke[165])

Substance	Temp. (°C.)	Time (minutes)	Equivalents required
Glycerol	50–60	15	8
Glucose	26	45	12
Sucrose	24	45	26
Cellulose	27	120	12
Biacetyl	24	5	2
Acetyl acetone	25	10	
Tartaric acid	26	10	
Malonic acid	26	10	
Citric acid	10	30	14
Malic acid	25	15	8

Glycerol: Smith and Duke[166] recommend the use of ceric perchlorate solution for the oxidation of glycerol to formic acid:

$$C_3H_8O_3 + 8Ce(ClO_4)_2 + 3H_2O \rightarrow 3HCOOH + 8Ce(ClO_4)_3 + 8HClO_4$$

Reagent: Dissolve 55–56 g. of $(NH_4)_2Ce(NO_3)_6$ by adding the salt to a liter beaker containing 340 ml. of 72 per cent perchloric acid. Stir well for a half minute interval and add 100 ml. of water. Continue this procedure until the total volume reaches 1 liter. Transfer to a suitable glass-stoppered bottle and store in the dark. The solution is standardized against sodium oxalate, nitroferroin being used as indicator (see p. 134).

Procedure: Add to the glycerol solution (free of other organic substances) a measured portion of standard ceric perchlorate solution which is known to be a sufficient excess. Dilute to 100 ml. with 4*N* perchloric acid. Warm on the steam bath to 50°C. and allow the reaction to proceed for 15 minutes at this temperature. The reaction temperature should not be allowed to exceed 60°C. Cool and titrate the excess of ceric ion with standard sodium oxalate solution, using 2 drops of 0.025*M* nitroferroin as indicator.

Notes: (1) If the use of perchloric acid is not permissible, sulfuric acid solutions may be used, but it is then necessary to heat to 90–100°C. for 90 minutes; the back-titration is done with Mohr's salt, ferroin being used as indicator.[167]

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[166] G. F. Smith and F. R. Duke, *Ind. Eng. Chem., Anal. Ed.*, **13**, 558 (1941).

[167] Cf. R. Cuthill and C. Atkins, *J. Soc. Chem. Ind.*, 57, 89 (1938); E. I. Fulmer, R. J. Hickey, and L. A. Underkofler, *Ind. Eng. Chem., Anal. Ed.*, 12, 729 (1940).

(2) Sharma and Mehrotra[168] have shown that, in the presence of a drop of 1 per cent chromium sulfate catalyst, glycerol and glycol are both oxidized by ceric sulfate to carbon dioxide and water. By oxidizing a mixture in this way and to the formic acid stage without a catalyst, it is possible to determine both components.

Other Hydroxy Compounds: Haslam and Ruddle[169] determine small amounts of tetrahydrofurfuryl alcohol in aqueous solution. They reflux a 10 ml. sample with 50 ml. of 0.1*N* ceric sulfate, 20 ml. of 6*N* sulfuric acid, and 50 ml. of water for 1 hour. The excess of ceric sulfate is back-titrated with a 0.1*N* solution of Mohr's salt, *N*-phenylanthranilic acid being used as indicator.

One milliliter of 0.1*N* ceric solution corresponds to 0.638 mg. of tetrahydrofurfuryl alcohol.

Methanol has been determined[170] by refluxing a 10–40 mg. sample for 10 minutes with 50 ml. of ceric nitrate solution (180 g. of ceric ammonium nitrate dissolved in 3 liters of water containing 270 ml. of concentrated nitric acid) and 1 ml. of 8*N* nitric acid for each 5 ml. sample. The excess of ceric ion is titrated with 0.1*N* sodium arsenite solution in the presence of 10 ml. of 6*N* sulfuric acid, 3 drops of 0.01*M* osmic acid, and 1 drop of ferroin indicator. Aldehydes, ketones, higher and aliphatic alcohols interfere.

Pentaerythritol may be determined by oxidation with excess of ceric perchlorate and back-titration with a standard oxalate solution.[171]

Hydroquinone: Furman and Wallace[172] showed that the reaction between ceric sulfate and hydroquinone is rapid and stoichiometric.

$$C_6H_4(OH)_2 \rightleftharpoons C_6H_4O_2 + 2H^+ + 2e$$

They recommend that the end-point be detected potentiometrically or with methyl red or diphenylamine as indicator. Various organic substances, particularly resorcinol and other polyhydric phenols, interfere by reacting with ceric salts. Kolthoff and Lee[173] also used ferroin as indicator and recommended the cerimetric assay of hydroquinone in preference to the iodine method except in cases where impurities likely to be oxidized by ceric sulfate are present.

Procedure: Weigh a sample of 0.6–0.8 g., transfer it to a 100 ml. graduated flask, dissolve in water, containing a little sulfuric acid, and dilute to the mark. Transfer 25 ml. to a 125 ml. Erlenmeyer flask, add indicator (Note

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[168] N. N. Sharma and R. C. Mehrotra, *Anal. Chim. Acta*, **13**, 419 (1955).

[169] J. Haslam and L. H. Ruddle, *Analyst*, **74**, 559 (1949).

[170] D. A. Skoog and Sister Monica (Marie Budde), *Anal. Chem.*, **25**, 822 (1953).

[171] L. Silverman, *J. Am. Oil Chemists' Soc.*, **25**, 359 (1948).

[172] N. H. Furman and J. H. Wallace, *J. Am. Chem. Soc.*, **52**, 1443 (1930).

[173] I. M. Kolthoff and T. S. Lee, *Ind. Eng. Chem., Anal. Ed.*, **18**, 452 (1946).

1), and titrate with ceric sulfate until the indicator changes color. Deduct the indicator correction.

Notes: (1) Two drops of aqueous 0.3 per cent barium diphenylaminesulfonate or 0.25 per cent diphenylamine in concentrated sulfuric acid (color change yellow to brown) or 1 drop of aqueous $0.025M$ ferroin (color change orange to yellow) can be used as indicator.

(2) There is little indication of the approach of the end-point; hence it is helpful if a "titration thief" is used.

(3) The indicator corrections are determined by titrating 50 ml. of water containing 0.2 g. of quinone, 25 meq. of sulfuric acid, and the indicator with $0.01N$ ceric sulfate solution. In the presence of quinone the correction was 0.02 ml. of $0.1N$ ceric sulfate; in its absence the correction was 0.01 ml.

(4) When several "low purity" samples were titrated in this way the results were similar to those obtained with the iodine method.

Benzoquinone: Schulek and Rózsa[174] made the interesting observation that addition of concentrated hydrochloric acid to an alcoholic benzoquinone solution yields a colorless solution. They claim that the quinone is reduced to dihydroquinone and an equivalent amount of ethanol is oxidized to acetaldehyde:

$$C_6H_4O_2 + C_2H_5OH \longrightarrow C_6H_4(OH)_2 + CH_3COH$$

The hydroquinone formed is titrated with ceric sulfate.

Procedure: Dissolve 1–50 mg. of benzoquinone (or quinhydrone) in a 100–200 ml. Erlenmeyer flask in 1–4 ml. of 96 per cent ethanol. Add all at once 5–10 ml. of concentrated hydrochloric acid to the solution and dilute immediately with water so that the acid concentration is 5 per cent. (If 5 ml. of conc. HCl was used, dilute with 35 ml. of water.) Add 1 drop of 0.2 per cent solution of *p*-ethoxychrysoidine in alcohol and titrate with 0.005–$0.05N$ ceric cerium solution until the red-orange color turns pure yellow. One milliliter of $0.05N$ cerium corresponds to 2.70 mg. of *p*-benzoquinone.

Notes: (1) The same investigators[175] determine α-tocopherols and certain of their derivatives by titrating 5 mg. samples dissolved in a mixture of 30 ml. of ethanol and 15 ml. of 10 per cent sulfuric acid, with $0.005N$ ceric sulfate, using *p*-ethoxychrysoidine as above.

(2) Quinone, of course, is also quantitatively reduced to hydroquinone by various metal reductors.

Carbohydrates: The determination of reducing sugars has been studied by a large number of investigators. Generally the procedures are based on treating the sample with an excess of Fehling's solution[176] or of alkaline ferricyanide[177] and then titrating the cuprous oxide or ferrocyanide produced in the reaction with ceric solution.

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[174] E. Schulek and P. Rózsa, *Z. anal. Chem.*, **121**, 258 (1941).

[175] E. Schulek and P. Rózsa, *Z. anal. Chem.*, **126**, 253 (1943).

[176] A. H. Best, A. H. Peterson, and H. M. Sell, *Ind. Eng. Chem., Anal. Ed.*, **14**, 145 (1942); R. A. Stegeman and D. T. Englis, *Trans. Ill. Acad. Sci.*, **27**, 75 (1934).

[177] H. C. Becker and D. T. Englis, *Ind. Eng. Chem., Anal. Ed.*, **13**, 15 (1941): **11**, 145 (1939); W. Z. Hassid, *ibid.*, **8**, 138 (1936); **9**, 228 (1937); R. B. Whitmoyer, *ibid.*, **6**, 268 (1934); R. Vanossi and R. Ferramola, *Anales asoc. quím. Argentina*, **23**, 162 (1935); B. F. Miller and D. D. Van Slyke, *J. Biol. Chem.*, **114**, 583 (1936); S. M. Strepkov, *Biochem. Z.*, **287**, 33 (1936).

The effects of various buffers and temperatures on the selective oxidation of dextrose and levulose by alkaline ferricyanide were studied by Englis and Becker,[177] who used $0.02N$ ceric sulfate with ferroin indicator for titrating the ferrocyanide formed. The best results in the oxidation step were obtained in presence of both sodium carbonate and disodium hydrogen phosphate. The former favors the oxidation of both sugars, whereas the latter retards the oxidation of dextrose. When 10 mg. of each sugar was taken, only about 7 per cent of the dextrose was oxidized under conditions which permitted complete oxidation of levulose. The original paper should be consulted for details; the method is not capable of great accuracy. The ferricyanide method has been used to obtain the reducing power of starches and dextrins.[178]

Birstein and Blumental[179] used direct oxidation with ceric sulfate and determined the excess iodometrically. Glucose, fructose, sucrose, and maltose were determined in this way. These authors also give a survey of earlier work and discuss the reaction mechanisms involved.

Forist and Speck[180] also recommend direct oxidation, but they use ceric perchlorate and oxidize at room temperature. The excess of ceric is determined by adding an excess of standard oxalate or arsenite and back-titrating with the ceric solution.

A method for the determination of sodium alginate by oxidation with an excess of ceric sulfate has been described by Gädeke;[181] silver sulfate is used to catalyze the reaction.

Unsaturated Compounds: Substances capable of undergoing an addition reaction with bromine can be determined, according to Sinn,[108] by treatment with excess of $0.1N$ ceric sulfate in the presence of bromide and acid (10 ml. of $5N$ hydrochloric acid or sulfuric acid in a volume of 150 ml.). After reaction, the solution is reduced with standard ferrocyanide and the excess of the latter is titrated with ceric sulfate.

Pyramidone: According to Percs and Lengyel,[182] pyramidone is readily oxidized by ceric sulfate to a stable product.

Procedure: Transfer 0.01–0.06 g. of sample to a 50 ml. flask, add 10 ml. of $5N$ sulfuric acid and 10 ml. of $0.1M$ ferric ammonium sulfate solution. A violet color appears; set the flask aside until the color disappears. Add 10 ml. of $0.1N$ ceric sulfate solution, 2 drops of ferroin, and titrate the excess with $0.1N$ ferrous sulfate solution. One milliliter of $0.1N$ ceric sulfate corresponds to 5.78 mg. of pyramidone. The oxidation may also be done with a standard solution of sodium vanadate.[183]

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[178] F. F. Farley and R. M. Hixon, *Ind. Eng. Chem., Anal. Ed.*, **13**, 616 (1941); W. Z. Hassid, R. M. McCready, and R. S. Rosenfels, *ibid.*, **12**, 142 (1940).

[179] G. Birstein and M. Blumental, *Bull. soc. chim. France*, **11**, 573 (1944).

[180] A. A. Forist and J. C. Speck, *Anal. Chem.*, **27**, 1166 (1955).

[181] A. Gädeke, *Z. anal. Chem.*, **131**, 428 (1950).

[182] E. Percs and J. Lengyel, *Magyar Kém. Lapja*, **4**, 536 (1949).

[183] V. M. Cherkasov and V. A. Petrova, *Zhur. Anal. Khim.*, **5**, 305 (1950).

8-Hydroxyquinoline: An empirical procedure for the determination of oxine with ceric nitrate in $2N$ perchloric acid solution is given by Gerber *et al.*[184]

Procedure: Dissolve the oxine in $2N$ perchloric acid and add an excess of 0.01–0.05N ceric nitrate in $2N$ perchloric acid. Heat the mixture for 15 minutes at 95–100°C. in an air-oven. Cool and back-titrate the excess of ceric cerium with standard oxalate solution, using a 0.1 per cent solution of setopaline C as indicator. Add the indicator near the end-point, the approach of which is shown by the fading of the ceric color to a very pale green. The final color change after the indicator has been added is from pink to colorless or yellow. Run a blank under the same conditions.

Determination of Metals as Oxines: Several methods have been proposed for the indirect determination of various metals by precipitation as the 8-hydroxyquinolate and oxidation of the latter with a ceric solution.

Nielsen[185] determined magnesium in biological materials in this way. A more favorable factor is obtained than with the bromination method, for 29.8 equivalents of cerium are consumed by 1 mole of 8-hydroxyquinoline. The empirical procedure described above for oxine can be applied to the determination of microquantities of magnesium.[184]

Procedure: Transfer a suitable volume of the magnesium solution to a 15 ml. conical centrifuge tube. Add a drop of phenol red and adjust the color (with hydrochloric acid and ammonia) until just yellow. Add 0.1 ml. of a 2 per cent solution of 8-hydroxyquinoline in 95 per cent ethanol for each 10 μg. of magnesium present, and then add dilute ammonia to a definite red color. Place the solution on the steam bath for 15–30 minutes. Cool, add 1 ml. of 95 per cent ethanol carefully to form a layer, and collect the precipitate by centrifuging. Wash the sediment three times with 3 ml. portions of N ammonia, each time placing a layer of alcohol on the wash liquid and centrifuging. After complete removal of vapors of alcohol by means of a slow current of air, dissolve the washed precipitate in 5 ml. of $2N$ perchloric acid and continue as described in the previous section.

One mole of magnesium corresponds to 59.5 equivalents of cerium.

It is even possible to determine 5 μg. of magnesium by the procedure.

Mehlig and Dernbach[186] determined aluminum by a similar procedure.

Zirconium may be determined indirectly after precipitation with tetra-*p*-chloro- or tetra-*p*-bromomandelic acid.[187] The reaction is:

$$\mathrm{Zr}(p\text{-}\mathrm{ClC_6H_4\cdot CHOHCOO})_4 + 8\mathrm{Ce(SO_4)} \qquad \mathrm{Zr(SO_4)_2} + \\ 4\mathrm{Ce_2(SO_4)_3} + 4\mathrm{CO_2} + 2\mathrm{H_2SO_4} + 4p\text{-}\mathrm{ClC_6H_4CHO}$$

Undoubtedly many metals which can be precipitated quantitatively as oxines could be determined in this way. In general, the bromometric procedure (p. 551) is preferable.

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[184] L. Gerber, R. I. Claassen, and C. S. Boruff, *Ind. Eng. Chem., Anal. Ed.*, **14**, 658 (1942).

[185] J. P. Nielsen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 649 (1939).

[186] J. P. Mehlig and C. J. Dernbach, *Chem. Anal.*, **32**, 80 (1943).

[187] M. R. Verma and S. D. Paul, *Nature*, **173**, 1237 (1954).

CHAPTER V

POTASSIUM DICHROMATE AS OXIDIZING TITRANT

1. **General Considerations.** Potassium dichromate is a less powerful oxidant than permanganate and is therefore more limited in its applications. However, it has some advantages; it serves as its own primary standard, the solution is stable indefinitely if properly stoppered,[1] acid solutions remain undecomposed when boiled, and ferrous iron may be titrated in the presence of moderate amounts of hydrochloric acid.

The use of potassium dichromate as a titrant was first proposed by Penny.[2] In his initial experiments he used potassium chromate, but found later that potassium dichromate was preferable because it was readily obtainable in a greater state of purity; he checked the equivalent against "harpsichord" wire. The method was applied to the determination of iron in ores and, later, to other determinations. Penny used potassium ferricyanide as an external indicator. Some attempts were made by later workers[3] to find a suitable internal indicator for this titration, but it was not until 74 years later that one having the necessary requirements was found, when Knop[4] introduced the use of diphenylamine. The general advantages of potassium dichromate as an oxidizing titrant were evidently appreciated because the method soon became widely accepted despite the inconvenience of using the external indicator. After Knop's important discovery, the reagent became of even greater practical value.

The standard oxidation potential of the dichromate system is 1.36 v.:

$$Cr_2O_7^{2-} + 14H^+ + 6e = 2Cr^{3+} + 7H_2O \qquad E^0 = 1.36$$

but the values for E^0 under the conditions normally used are less than this. Smith and his coworkers[5] have reported the values (the so-called formal potentials) given in Table I. These results should be taken into account when the suitability of any particular indicator is being considered for the titration of ferrous solutions with dichromate.

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[1] Cf. W. M. Carey, *J. Am. Pharm. Assoc.*, 16, 115 (1927).

[2] F. Penny, *Brit. Assoc. Advancement Sci. Rept.*, **18** [2], **58** (1850); cf. E. R. Caley and H. K. Anders, *J. Chem. Educ.*, 26, 203 (1949).

[3] P. Cazeneuve, *Chem. Ztg.*, **24**, 684 (1900); L. Brandt, *Z. anal. Chem.*, **45**, 95 (1906); **53**, 1 (1914).

[4] J. Knop, *Z. anal. Chem.*, **63**, 96 (1923); *J. Am. Chem. Soc.*, 46, 263 (1924).

TABLE I

Acid Present	$Cr_2O_7^{2-}/Cr^{3+}$ (E^0, in volts)	Fe^{3+}/Fe^{2+} (E^0, in volts)
0.1M HCl	0.93	0.73
1M HCl	1.00	0.70
2M HCl	1.05	0.69
4M HCl	1.10	0.66
1M H_2SO_4	1.03	0.69
2M H_2SO_4	1.11	0.688
4M H_2SO_4	1.15	0.687
8M H_2SO_4	1.35	0.658
1M $HClO_4$	1.025	0.735

Detection of the End-Point: It has already been stated that potassium ferricyanide used as an external indicator was the first reagent to be applied in the detection of the end-point. In a recent examination of this indicator, Stockdale[6] found that its critical potential is slightly lower than that required by diphenylamine. He concluded that potassium ferricyanide ceased to give a blue color when about 1 part per thousand of ferrous iron remained unoxidized. This opinion was confirmed when the results were compared with those obtained with suitable internal indicators, for they were always about 0.2 per cent lower. Accordingly, it is only possible to obtain exact results with ferricyanide when the dichromate solution is standardized against a known ferrous solution of similar concentration to that being analyzed.

The use of diphenylamine[4] is also fraught with uncertainties. Sometimes irregular results are obtained and green or yellow or red colors are formed at the end-point. The mechanism of the oxidation has already been discussed in Volume I, pp. 133–134. Diphenylbenzidine is first produced, and this in turn is oxidized to diphenylbenzidine violet; the green color is caused by the formation of a slightly soluble addition compound of diphenylbenzidine and diphenylbenzidine violet which occurs if an undue excess of indicator is used. Diphenylbenzidine violet can also be irreversibly oxidized by an excess of oxidizing agent to produce red or yellow compounds of unknown composition. This happens particularly when the titration is done at low acidities (above pH 2); it is also more marked with increase in temperature.

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[5] G. F. Smith and F. P. Richter, *Ind. Eng. Chem., Anal. Ed.*, 16, 580 (1944); G. F. Smith, *Anal. Chem.*, 23, 925 (1951); cf. H. H. Willard and G. D. Manalo, *ibid.*, 19, 462 (1947).

[6] D. Stockdale, *Analyst*, 75, 150 (1950).

The oxidation of the indicator is normally slow but is induced by the reaction between dichromate and ferrous iron. Accordingly, it is preferable to determine the indicator correction by comparison with the potentiometric titration[7] rather than by treating a solution containing the indicator, but no ferrous ions, with a dilute solution of potassium dichromate until the color change is obtained. The redox potential of the indicator is less than that of the ferrous-ferric couple near the end-point; hence the color change is not sharp and occurs too soon owing to partial oxidation. The addition of phosphoric acid is therefore necessary; it lowers the oxidation potential of the ferrous-ferric system by forming a complex with the ferric ion. Stockdale,[6] however, obtained good results without this addition and commented that the omission of phosphoric acid was to be preferred because a better warning of the end-point approach was obtained.

Since diphenylbenzidine is formed intermediately in the oxidation of diphenylamine, the direct use of diphenylbenzidine would be expected to serve the same purpose with the added advantage of lowering the indicator correction. This was found to be so,[8] but the main objection to the use of diphenylbenzidine is its very low solubility (0.06 mg. per liter of water). When diphenylbenzidine is formed during a titration by the oxidation of diphenylamine, most of it forms a colloidal suspension which readily reacts with the oxidant when the required potential is reached. When diphenylbenzidine (dissolved in concentrated sulfuric acid) is used directly, it coagulates as soon as it is added to the ferrous solution; this form of the indicator reacts very slowly with excess of oxidant and the end-point may be passed before the color change appears. Stockdale[6] noted that the redox potential of diphenylbenzidine appeared to be about 0.06 v. higher than that of diphenylamine when the electrometric titration was done at a practicable rate, whereas it should have been the same. He attributed this to the difficulty of obtaining an equilibrium because of the insoluble nature of diphenylbenzidine.

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[7] N. H. Furman, *Ind. Eng. Chem.*, 17, 314 (1925); I. M. Kolthoff and L. A. Sarver, *J. Am. Chem. Soc.*, 53, 2902, 2906 (1931).

[8] I. M. Kolthoff and L. A. Sarver, *J. Am. Chem. Soc.*, 52, 4179 (1930).

Neither diphenylamine nor diphenylbenzidine can be used in the presence of tungstate, which reacts to form acid-insoluble compounds. Sarver and Kolthoff[9] recommended a new indicator, diphenylaminesulfonic acid, which can be used in presence of tungstates. A further advantage is that the indicator, in the form of its barium or sodium salt, is soluble in water. The oxidation mechanism is similar to that of diphenylamine, but the color of the oxidized indicator is reddish violet. The change occurs at 0.85 v. (i.e., nearly 0.1 v. higher than diphenylamine). Sarver and von Fischer[10] found that sodium diphenylbenzidinepolysulfonate resembles the diphenylamine sulfonate in properties (cf. Vol. I), but this indicator does not appear to have found much application.

All these indicators may also be used in the titration of dichromate with ferrous solutions, but the titration should be done without delay because of the risk of irreversible oxidation. Diphenylaminesulfonic acid is less resistant to oxidizing agents than diphenylamine or diphenylbenzidine; for example, a solution of dichromate containing diphenylbenzidine can be titrated without error even if it has been set aside for 15 minutes, but when a solution containing diphenylaminesulfonic acid is treated similarly appreciable errors can arise. No differences are observed if the titration is done immediately; hence diphenylaminesulfonic acid, because of its other advantages, is often preferred.

N-Methyldiphenylaminesulfonic acid[11] is said to be better than diphenylaminesulfonic acid because the oxidized form is more stable and the indicator correction is smaller. The color change from colorless to purple-red is very sensitive and enables satisfactory end-points to be obtained even when $0.005N$ solutions are used. A 0.1 per cent aqueous solution of the sodium salt is used. Critical studies of the applications of this indicator have yet to be reported. The oxidation potential is 0.80 v.

N-Phenylanthranilic acid is said to be a useful indicator;[12] the oxidation potential (1.08 v.) is higher than that of diphenylamine-sulfonic acid and the addition of phosphoric acid is unnecessary. The color change is from colorless to pink. In view of its potential, which is even higher than that of ferroin, it would be surprising if this indicator behaved satisfactorily in the titration of ferrous iron with dichromate even at the acidity of greater than $2N$ which was recommended by the originators (cf. p. 127). Furness[13] noted that it gave a less satisfactory color change than diphenylamine-sulfonic acid; his acidity was of the order of 2–$3N$. Belcher[14] found that the color change was unsatisfactory in 2–$4N$ acid solutions. *N*-Phenylanthranilic acid is more suitable for titrations with ceric sulfate (p. 126), where it would be expected to function better in view of the higher potentials of the systems involved.

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[9] L. A. Sarver and I. M. Kolthoff, *J. Am. Chem. Soc.*, **53**, 2902, 2906 (1931).

[10] L. A. Sarver and W. von Fischer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 271 (1935).

[11] J. Knop and O. Kubelkova-Knopova, *Z. anal. Chem.*, **122**, 183 (1941).

[12] V. S. Syrokomskii and V. V. Stiepin, *J. Am. Chem. Soc.*, **58**, 928 (1936); *Zavodskaya Lab.*, **5**, 144 (1936).

o-Phenanthroline-ferrous sulfate (ferroin), which yields such excellent results in titrations with ceric sulfate (p. 124), is less satisfactory with dichromate under the usual conditions of acidity. This is due to the fact that its redox potential (1.06 v.) is too high for the dichromate-ferrous system unless the acidity is raised to fairly high concentrations (cf. Table I). Stockdale[6] obtained good results in $2.5N$ sulfuric acid solutions, but from Table I one would expect a higher concentration to be necessary; Smith and Brandt[15] state 5–$6M$. The same remarks apply to 5-methylferroin (1.02 v.). Both indicators are, however, satisfactory in the reverse titration, i.e., of dichromate with ferrous solutions, because the reverse titration follows a slightly different course, as can be shown by potentiometric titration. When dichromate is titrated with ferrous solution in $1M$ sulfuric acid, the equivalence potential lies between 1.22 and 0.85 v., whereas, when the reverse titration is done, the equivalence potential lies between 0.85 and 1.0 v.[15] Accordingly in the titration of dichromate with ferrous, the redox potential of ferroin lies within the range of the equivalence potential and so functions satisfactorily.

Some of the substituted dipyridyls and *o*-phenanthrolines have been reported on favorably. Smith and Brandt[15] strongly recommend the use of 5,6-dimethylferroin, which has a redox potential of 0.97 v. in $1M$ acid. The color change is from orange to green in the presence of hydrochloric acid (without phosphoric acid) and from red to yellow-green in the presence of sulfuric acid. Both the oxidized and reduced forms are very stable. The end-points are very sharp when 0.05 ml. of 0.025*M* dimethylferroin is used in a titration volume of 150 ml. The sharpness of the color change is not affected after 30 reversals of the end-point. This indicator is said to be the best available for the titration of ferrous iron with dichromate.

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[13] W. Furness, *Analyst*, **75**, 2 (1950).

[14] R. Belcher, Unpublished studies.

[15] G. F. Smith and W. W. Brandt, *Anal. Chem.*, **21**, 948 (1949).

For titrations at low acidity (0.1–0.5*N*), 3,4,7,8-tetramethylferroin (0.85 v. in 0.1*M* acid) and 4,7-dimethylferroin (0.88 v. in 0.5*M* acid) have been recommended.[16] The color changes are even more intense than with 5,6-dimethylferroin.

Dwyer and Gibson[17] examined 2,2′-dipyridyl osmium(II) perchlorate and the corresponding phenanthroline compound as indicators in the dichromate-ferrous titration. The latter gave better end-points (yellow-green to blue-green) and was recommended for this titration; the redox potential was found to be 0.86 v. An acidity of 1*N* in sulfuric acid was recommended for the titration and phosphoric acid was added.

Several other indicators have been recommended but have not come into general use. Among these may be mentioned *p*-phenetidine,[18] *o*-dianisidine,[19] naphthidine,[20] *m*- and *p*-tolylphenylamine,[20] diaminodiphenylamine,[21] *m*- and *p*-anilinobenzoic acid,[22] sulfonated diphenylamine,[20] pyrogallol,[23] and brucine sulfate.[24]

Some other indicators are described in Volume I, pp. 135–136, and in Chapter I, p. 27.

Diphenylaminesulfonic acid is probably the best indicator for general purposes. In the methods to be described later in this chapter, we have retained the particular indicator recommended by the investigators quoted. It can be assumed however, that diphenylaminesulfonic acid may be used to advantage in their stead in most instances. It would be desirable for authors to give their experiences with 5,6-dimethylferroin as indicator.

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[16] G. F. Smith, *Anal. Chem.*, **23**, 925 (1951).

[17] F. P. Dwyer and N. A. Gibson, *J. Proc. Roy. Soc. N.S.W.*, **84**, 83 (1950).

[18] L. Szebellédy, *Z. anal. Chem.*, **81**, 95 (1930).

[19] M. E. Weeks, *Ind. Eng. Chem., Anal. Ed.*, **4**, 127 (1932); G. Milazzo and L. Paolini, *Mikrochemie*, **36/37**, 255 (1951).

[20] L. E. Straka and R. E. Oesper, *Ind. Eng. Chem., Anal. Ed.*, **6**, 465 (1934); cf. S. Cohen and R. E Oesper, *ibid.*, **8**, 306, 364 (1936); R. Belcher, A. J. Nutten, and W. I. Stephen, *J. Chem. Soc.*, **1952**, 3857.

[21] L. P. Hammett, G. H. Walden, and S. M. Edmonds, *J. Am. Chem. Soc.*, **56**, 1092 (1934).

[22] V. M. Cherkasov, *Zhur. Obshcheĭ Khim.*, **23**, 121, 197 (1953).

[23] A. B. Dutta, *Current Sci. (India)*, **24**, 97 (1955).

[24] S. Miyagi, *J. Soc. Chem. Ind. Japan*, **36**, Suppl. binding 146 (1933).

Stock Solutions of Commonly Used Indicators. *Diphenylamine and diphenylbenzidine:* These are generally prepared by dissolving 1 g. of the compound in 100 ml. of concentrated sulfuric acid. Less often, solutions one fifth or one tenth of this strength are used. In all subsequent discussions the "1 per cent" solution is referred to unless otherwise specified.

Diphenylaminesulfonic acid is generally used as a 0.2 per cent solution of the barium salt in water. An equivalent concentration of the sodium salt may be used.

N-Phenylanthranilic acid: The solution is usually prepared by dissolving 0.1 g. of the compound in an equivalent amount of sodium carbonate solution; this preparation is not stable indefinitely. Bishop and Crawford[25] state that a more stable solution is obtained by dissolving 0.25 g. in 12 ml. of $0.1N$ sodium hydroxide and diluting to 250 ml. with water. The method recommended by Clark[26] is also of interest. He prepared a 5 per cent solution in molten urea and added a suitable amount of the powdered solid to the test solution.

5,6-Dimethylferroin: A $0.01M$ solution is prepared from 0.03 mole of the dye base with the theoretical amount of $0.01M$ ferrous sulfate heptahydrate.

Indicator Corrections (Titration of ferrous iron with dichromate): For each 0.1 ml. of "1 per cent" diphenylamine, deduct a correction of 0.05 ml. of $0.1N$ dichromate, and for each 0.1 ml. of 0.2 per cent diphenylaminesulfonic acid deduct 0.01 ml. of $0.1N$ dichromate; this correction is the theoretical value. However, the indicator corrections depend somewhat on the experimental conditions and it is therefore advisable to determine the correction under the conditions which are used. This injunction applies particularly when dichromate is titrated with ferrous solution; the indicator must always be added at the same stage in every titration and the operation should always be completed without delay.

In titrations with solutions $0.03N$ or stronger, the indicator correction for *N*-phenylanthranilic acid is negligible.

Because the indicator correction for diphenylaminesulfonic acid is quite large, Willard and Young[27] recommended the use of the oxidized form of the indicator for titrations with ferrous solutions. A suspension of the oxidized indicator can be prepared as follows:

> Dilute 100 ml. of $0.01M$ sodium diphenylaminesulfonate and 5 ml. of concentrated sulfuric acid to 300 ml. and slowly add 25 ml. of $0.1N$ dichromate followed by 8 ml. of $0.1N$ ferrous sulfate. Set aside the green mixture for 3–4 days until a sample of the supernate gives no color with 100 ml. of water containing 2 ml. of $0.1N$ dichromate and 5 ml. of concentrated sulfuric acid. Carefully siphon off the supernate, add 300 ml. of water and 15 ml. of concentrated sulfuric acid, and siphon again after the precipitate has settled. Centrifuge and wash the pre-

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[25] E. Bishop and A. B. Crawford, *Analyst*, **74**, 365 (1949).

[26] R. E. D. Clark, *Nature*, **168**, 876 (1951).

[27] H. H. Willard and P. Young, *Ind. Eng. Chem., Anal. Ed.*, **5**, 154 (1933).

cipitate. Shake the washed precipitate with 100 ml. of water and use the suspension as a stock solution. One milliliter of the suspension after the oxidation has the same color intensity as 0.6 ml. of $0.01M$ diphenylaminesulfonic acid.

Willard and Young[27] determined the indicator corrections for the titration of chromate (and vanadate) with ferrous sulfate in the presence of phosphoric acid or hydrofluoric acid and sulfuric acid. The corrections were 0.37, 0.95, and 1.42 ml. of $0.01N$ ferrous solution for 0.3, 0.6, and 0.9 ml. of suspension when phosphoric and sulfuric acids were present; when hydrofluoric acid was used instead of phosphoric acid, the corrections were slightly greater. The correction for vanadate titration is slightly less than for chromate titration; this is explained by the stronger oxidizing action of chromic acid which thus destroys more indicator than vanadate.

For convenience, some of the properties of the important indicators are listed in Table II.

TABLE II

Indicators Recommended for Dichromate-Ferrous Titrations

Indicator	E^0 Value	Amt. per titration with $0.1N$ Soln.	Color change Reduced form	 Oxidized form
Diphenylamine	0.76	3 drops/200 ml.	Colorless (green)	Violet
Diphenylbenzidine	0.76	3 drops/200 ml.	Colorless (green)	Violet
Diphenylamine-sulfonic acid	0.84	7–10 drops/150 ml.	Colorless (green)	Reddish violet
5,6-Dimethylferroin	0.97	1 drop/150 ml.	Red	Yellow-green
N-Phenylanthranilic acid	1.08[a]	10 drops	Colorless (green)	Pink

[a] Cf. p. 127.

Preparation of Pure Potassium Dichromate (equivalent weight, 49.04; rational weight, 49.03): The commercial product is thrice recrystallized from water and dried at 200°C. or, better, fused in an electric oven. It can be stored without decomposition.

Purity Tests. *Water:* Ten grams of potassium dichromate should not lose more than 1 mg. in weight on fusion in an electric oven (1:10,000). After drying at 200°C., the water content is less than 0.01 per cent.

Sulfate: The commercial product usually contains sulfate. To 10 ml. of 6 per cent potassium dichromate are added 6 drops of $4N$ hydrochloric acid and 2 ml. of $0.5N$ barium nitrate. After 20 minutes, there should be no perceptible turbidity or opalescence (1 SO_4:10,000 $K_2Cr_2O_7$). (The sulfate reaction is less sensitive in hydrochloric than in acetic acid solutions; mineral acid must be used here to avoid precipitation of barium chromate.)

Chloride: Five milliliters of a 6 per cent solution should show no turbidity or opalescence after the addition of 2 ml. of 4*N* nitric acid and silver nitrate (0.2 KCl: 10,000 $K_2Cr_2O_7$).

Chromic Acid: Even good commercial products often contain chromic acid as an active impurity; 0.1 per cent CrO_3 raises the effective strength by 0.047 per cent.

The intense orange-yellow color of dichromate solutions makes the detection of free chromic acid by color indicators difficult. It is, however, possible to detect 0.1 per cent of CrO_3 in a 4 per cent solution of potassium dichromate with 2,4-2′,4′-2″,4″-hexamethoxytriphenylcarbinol. It is better to carry out a conductivity titration in which chromic acid as well as chromate can be determined in potassium dichromate. When the solution is titrated with alkali, the conductivity decreases until the chromic acid is converted to dichromate. On further addition, the conductivity alters but slightly. A sharp break is obtained when the values are plotted graphically. Alternatively, the chromate can be titrated with acid. The conductivity alters only slightly until the chromate is converted to dichromate when a large increase occurs. Preferably, a 2 per cent dichromate solution is titrated with alkali (or acid) from a microburette. In testing various commercial products, Kolthoff has found the following values: Product I, 0.80 per cent CrO_3; Product II, 1.2 per cent CrO_3; II thrice recrystallized, 0.00 per cent CrO_3; Kahlbaum product, 0.24 per cent CrO_3.

Preparation of 0.1N Potassium Dichromate: Weigh out 4.903 g. of the pure dry salt, dissolve in water, and dilute to 1000 ml.

2. Methods for Inorganic Compounds. ***Ferrous Iron:*** The titration of ferrous iron with dichromate has already been referred to in the discussion of indicators (p. 170). Knop,[4] of course, used diphenylamine as indicator, but diphenylaminesulfonic acid,[9] in the form of either its sodium or barium salt, is to be preferred.

One of the main advantages of potassium dichromate as a titrant for ferrous iron is that moderate amounts of hydrochloric acid do not interfere, as they do with permanganate. In general practice, a concentration of 1–2*N* is used, but, according to Tsubaki,[28] a higher concentration (3.5*N*) can be tolerated.

Procedure: To 25 ml. of the ferrous solution add 10 ml. of 4*N* sulfuric acid or hydrochloric acid, 5 ml. of syrupy phosphoric acid, and 6–8 drops of a 0.2 per cent solution of sodium diphenylaminesulfonate in water. Titrate with 0.1*N* dichromate solution. About 0.5 per cent before the end-point, the green color deepens and the titration is continued carefully to the violet-blue end-point. Overtitration can easily be avoided by titrating first without phosphoric acid to dark green (1.5 per cent before the end-point) and then adding the phosphoric acid and finishing as before.

Notes: (1) In the presence of phosphoric acid, the color change is easily reversible. Dichromate can thus be titrated with ferrous solution in the presence of diphenylaminesulfonic acid, but the indicator is slowly destroyed in the presence of excess of oxidizing agent. Accordingly, the titration should be done quickly (p. 172).

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[28] I. Tsubaki, *Japan. Analyst*, **3**, 253 (1954).

(2) The other indicators which can be used instead of diphenylaminesulfonic acid have been considered in the section on indicators (p. 170).

(3) Citric, tartaric, and oxalic acids interfere with the dichromate titration of ferrous iron,[29] but up to 2 g. of succinic acid are without effect. Glucose also interferes.[30]

(4) Ferrous iron can be titrated in the presence of as much as 0.1 g. of thiocyanate with either dichromate or permanganate provided that sufficient mercuric nitrate is present to yield one Hg^{2+} for one CNS^-.[31] In the dichromate titration, the mercuric nitrate solution is added quickly followed by 5 ml. of 90 per cent phosphoric acid and 3 drops of 1 per cent diphenylamine indicator; the titration is completed to a violet color. For the permanganate titration, the mercuric nitrate solution is added followed by 10 ml. of a solution containing 200 ml. of 90 per cent phosphoric acid, 70.5 g. of manganous sulfate, 10 ml. of concentrated sulfuric acid, and 500 ml. of water; 3 drops of diphenylamine indicator are added before the titration.

(5) For the determination of ferrous ion in difficultly soluble materials, Seil[32] makes use of the fact that on heating a ferrous compound with concentrated sulfuric acid quantitative oxidation to ferric iron occurs with formation of an equivalent amount of sulfur dioxide:

$$2FeSO_4 + 2H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + SO_2 + 2H_2O$$

Seil passes the sulfur dioxide evolved through two wash bottles which contain measured volumes of 0.1*N* standard dichromate solution. (Seil assumes that the sulfur dioxide is quantitatively oxidized to sulfuric acid, but does not present any experimental evidence to substantiate this.) The excess of dichromate is back-titrated by one of the conventional methods. For details the original article should be consulted. The methods fail if the sample contains carbon, sulfide, metals, or any reducing agent other than ferrous oxide, for these will also liberate sulfur dioxide from the sulfuric acid.

Applications of the Ferrous Titration: Ferrous iron in acid or alkaline solutions is often used for the reduction of oxidizing substances. When the reaction is not instantaneous, an excess is added and is back-titrated after the main reaction has gone to completion. Dichromate is the standard solution which has been most commonly used for the back-titration, but other standard oxidizing agents, such as permanganate (p. 79), ceric sulfate (p. 147), or vanadate (p. 634), can be used in most instances. When organic substances are present, the authors recommend ceric sulfate instead of dichromate for the back-titration.

The titration of ferrous iron also finds application in the determination of the reduced forms of some metals which can be oxidized by ferric iron. The ferrous iron produced is then titrated. Copper (see below) and uranium (p. 189) come into this category.

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[29] M. I. Neevel, University of Minnesota, unpublished work.

[30] E. Bishop and A. B. Crawford, *Analyst*, 75, 273 (1950).

[31] F. Burriel-Marti and F. Lucena-Conde, *Anales real soc. españ. fís. y quím. (Madrid)*, 44B, 95 (1948).

[32] G. E. Seil, *Ind. Eng. Chem., Anal. Ed.*, 15, 188 (1943).

Copper: Cuprous copper is usually determined by allowing it to react with a ferric salt and then titrating the equivalent amount of ferrous iron which is produced. Hatch and Estes[33] assayed cuprous chloride in this way.

Procedure: Transfer 0.3 g. of cuprous chloride to a dry 500 ml. Erlenmeyer flask and add 25 ml. of ferric ammonium sulfate solution (10 g. dissolved in sufficient N hydrochloric acid to give 100 ml. of solution). Swirl the contents of the flask until the solid has dissolved. Add 300 ml. of a solution containing 80 ml. of concentrated sulfuric acid and 25 ml. of phosphoric acid per liter, and 5 drops of 2 per cent barium diphenylamine sulfonate as indicator. Titrate with $0.1N$ dichromate.

Carry out blank determination.

Note: Permanganate and ceric sulfate titrations were also tried. The dichromate procedure is recommended for general purposes, but when the highest accuracy is required ceric sulfate titration (p. 152) is to be preferred.

Many alternative titrimetric methods have been described for completing the determination of copper after having precipitated it as cuprous thiocyanate; all require that the precipitate first be filtered off. Burriel and Lucena,[34] however, have found a means of avoiding this step. The cuprous salt is oxidized with ferric sulfate, and the ferrous iron so produced is titrated with dichromate; the interference of ferrithiocyanate ions is eliminated by the addition of a mercuric salt.

Procedure: Fit a 500 ml. conical flask with entry and exit tubes. It is convenient if the entry tube is fitted with a three-way tap to simplify the change-over from sulfur dioxide to carbon dioxide. In the flask place the neutral or slightly acid solution, free from oxidizing agents, and containing about 0.15 g. copper as sulfate. Dilute to 200–250 ml. and saturate with sulfur dioxide in the cold. Continue to pass sulfur dioxide, bring just to boiling, and add $0.2N$ potassium thiocyanate solution drop by drop from a burette, shaking continuously, until precipitation is complete. Note the volume of precipitant used. The precipitate should be completely white, and the supernatant liquid should be colorless. A permanent greenish yellow color indicates incomplete removal of oxidizing agents, or too high an acidity.

When precipitation is complete, pass a rapid stream of carbon dioxide, washed with potassium permanganate, through the solution until the issuing gas no longer decolorizes a dilute acid solution of permanganate. Allow the solution to cool to room temperature and continue the passage of carbon dioxide. Add 25 ml. of sulfuric acid (1:4). Add drop by drop, while shaking vigorously, a $0.5M$ solution of ferric sulfate until all the precipitate has dissolved, giving a solution strongly colored with ferric thiocyanate.

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[33] L. F. Hatch and R. R. Estes, *Ind. Eng. Chem., Anal. Ed.*, **18**, 136 (1946).
[34] F. Burriel-Marti and F. Lucena-Conde, *Anal. Chim. Acta*, **2**, 230 (1948).

Add in one portion a volume of $0.2M$ mercuric nitrate or mercuric thiocyanate solution equal to the volume of potassium thiocyanate used as precipitant. The red color is replaced by the green color of the mixture of copper(II) and excess iron(III). Add 10 ml. of phosphoric acid (sp. gr. 1.75), which leaves only the blue of copper(II). Add 3 drops of 1 per cent solution of diphenylamine in concentrated sulfuric acid, and titrate immediately with $0.1N$ potassium dichromate solution.

One milliliter of $0.1N$ potassium dichromate corresponds to 6.357 mg. of copper.

Carry out a blank determination.

Notes: (1) The error is always less than 0.4 per cent.

(2) The carbon dioxide atmosphere is essential to prevent atmospheric oxidation of ferrous iron which is catalyzed by cupric ions.

(3) Appreciable amounts of chloride interfere owing to the formation of mercuric chloride.

(4) A modified form of the method has been applied to the determination of copper in alloys.[35]

(5) Mercury(I) may be determined by a similar procedure.[36]

Chromium: Chromium is determined by oxidizing to chromate with ammonium persulfate. Excess of ferrous iron is then added and back-titrated. The following method has been described for the analysis of ferrochromium.

Procedure:[37] Transfer 0.4 g. of the sample to an 800 ml. conical beaker. Add 25 ml. of 1:1 sulfuric acid, cover the beaker, and heat very gently for 20 minutes or until action has apparently ceased. Add 20 ml. of 1:1 phosphoric acid, cover the beaker, and evaporate just to fuming. Allow to cool, add 40 ml. of cold water, bring to a boil, add 1 ml. of concentrated nitric acid, and boil for 2 minutes.

Dilute to 400 ml. with hot water, add a few pieces of crushed silica brick (or glass beads), 1 ml. of a 0.5 per cent solution of potassium permanganate, 25 ml. of 1 per cent silver nitrate solution, and 6 g. of ammonium persulfate. Heat to boiling and boil for 10 minutes after the permanganate color develops. Add 15 ml. of 1:3 hydrochloric acid to destroy the permanganate (if this is insufficient add further 5 ml. portions), boil for 5 minutes more, and cool to room temperature.

Titrate with $0.2N$ ferrous ammonium sulfate solution until the solution turns green; then add at least 5 ml. in excess. Add 5 drops of barium diphenylaminesulfonate indicator (0.37 g. dissolved in 90 ml. of hot water and diluted to 100 ml. when cool) and titrate the unconsumed ferrous ammonium sulfate with $0.1N$ potassium dichromate solution.

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[35] F. Burriel-Marti and F. Lucena-Conde, *Anales real soc. españ. fís. y quím.* (*Madrid*), **47B**, 459 (1951).

[36] *Idem, ibid.*, **46B**, 169 (1950).

[37] British Standard 1121: Part 18: 1951.

Standardization: Transfer 25 ml. of 1:1 sulfuric acid and 20 ml. of 1:1 phosphoric acid to an 800 ml. conical beaker, dilute to 400 ml., and add 5 drops of indicator solution. Add 3 drops of $0.2N$ ferrous ammonium sulfate and titrate carefully with $0.1N$ potassium dichromate solution until the first appearance of a deep violet color. Add 40 ml. of $0.2N$ ferrous ammonium sulfate solution and titrate with $0.1N$ potassium dichromate to the deep violet end-point. Calculate the normality of the ferrous ammonium sulfate from the amount of $0.1N$ potassium dichromate solution consumed by the 40 ml.

Notes: (1) The method is suitable for both high and low carbon grades of the usual commercial types of ferrochromium alloy but is not recommended for special types containing more than 4 per cent of silicon. High carbon grades should be crushed to pass a 60 mesh sieve; where the alloy crushes readily (i.e., when there is no risk of contamination from the crushing medium) the sample may be advantageously crushed through a 90 mesh sieve. Low carbon grades can be prepared as fine drillings or millings which may then have to be rubbed in a hardened steel mortar to reduce their size sufficiently to pass a 30 mesh sieve.

(2) The whole of the sample should be covered by the acid; the beaker should be disturbed as little as possible during the dissolution to avoid fine particles becoming stranded on the walls.

(3) If the permanganate color does not develop after boiling for 5 minutes, cautiously add further 0.5 g. amounts of ammonium persulfate. Boil for 10 minutes after the color appears.

(4) When vanadium is present, $0.1N$ permanganate is used in place of dichromate. The indicator is then omitted and the end-point is taken to a "violet" color (permanganate pink plus chromium green) which persists for at least 30 seconds.

Permanganate end-points are difficult to locate in a chromium-rich solution; hence dichromate is to be preferred where possible.

Cobalt: Cartledge and Nichols[38] oxidize the cobalt to green trioxalatocobaltiate. This is reduced with a slight excess of standard ferrous sulfate and the ferrous iron is back-titrated with dichromate.

Procedure: Add to 10–25 ml. of about $0.05M$ neutral cobalt solution, 2 ml. of glacial acetic acid, 5 ml. of 20 per cent ammonium acetate, 10 ml. of M potassium oxalate, and about 1 g. of manganese-free lead dioxide. Set aside for 5–10 minutes in diffuse light and shake occasionally. Filter, wash, and add standard ferrous sulfate to the filtrate to give about 0.5 ml. in excess (shown by a color change from green to yellow). Set aside for 5 minutes, add 1 ml. of a solution containing 10 ml. of phosphoric acid and 25 ml. of sulfuric acid in 100 ml., and dilute to about 75 ml. Add 3 drops of 1 per cent diphenylamine solution and titrate with standard $0.05N$ potassium dichromate. Not more than 1.0 ml. should be used. Read the two burettes and add to the mixture as much ferrous sulfate as is estimated to be about equivalent to the dichromate consumed in the back-titration. Again titrate with dichromate.

Notes: (1) The titration of ferrous iron with dichromate in the presence of oxalate is not accurate. Therefore the ratio between the ferrous sulfate and dichromate solutions, under the conditions prevailing near the end-point, is calculated from the supplementary titration.

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[38] G. H. Cartledge and P. M. Nichols, *Ind. Eng. Chem., Anal. Ed.*, 13, 20 (1941).

(2) Manganese, which yields an unstable trioxalatomanganate, interferes.

Léontovich and Bénard[39] required a method for the determination of cobalt in oxide coatings. They precipitate potassium cobaltinitrite and oxidize the washed precipitate with an excess of standard dichromate solution. Iron, copper, and nickel do not interfere.

Procedure: Dissolve the sample in 20 ml. of water and add 5 ml. of acetic acid, 10 ml. of 40 per cent sodium nitrite, and 10 ml. of 10 per cent potassium sulfate. Set aside for 12 hours. Centrifuge and siphon off the supernate. Suspend the precipitate in the potassium sulfate solution, centrifuge and siphon; repeat this 2–3 times. Add to the precipitate 20 ml. of 0.4N potassium dichromate and 10 ml. of 1:1 sulfuric acid. Heat at 60°C. until dissolution is complete. Transfer the solution to a 500 ml. beaker, add 15 ml. of a solution containing 150 ml. of sulfuric acid ($d = 1.84$) and 150 ml. of phosphoric acid ($d = 1.75$) per liter, and 2 drops of 0.025M ferroin, and dilute to 200 ml. Titrate with 0.1N ferrous ammonium sulfate.

Note: A similar titration of potassium cobaltinitrite precipitates has been recommended for the determination of nitrite.[40]

The method of Willard and Hall[41] in which a potentiometric titration is used has been modified by Gillis and Cuvelier[42] who used diphenylamine as indicator. Cobalt(II) is oxidized to cobalt(III) with sodium perborate; the excess of oxidant is destroyed by boiling. A standard solution of stannous chloride is added in excess and is back-titrated with standard dichromate. An atmosphere of carbon dioxide is maintained during the reduction and final titration. The indicator must not be added until the end-point is near, and it is necessary to establish this by a preliminary assay. The method is applicable in the presence of nickel and small amounts of iron.

Nitrate: Various reductimetric methods have been described in the literature for the determination of nitrate. Usually, however, a complicated apparatus is necessary and the methods are time-consuming, often inexact, and subject to interference from aerial oxygen. Moreover, the different reagents do not react with nitrate in simple stoichiometric ways but give rise to the formation of different nitrogen oxides. Kolthoff found that hydrazine sulfate, arsenious acid, and antimony trichloride are unsuitable for the titrimetric determination of nitrate because the reactions have very complicated mechanisms and quantitatively are very dependent on the reaction conditions. The iodometric method, which is based on the reducing action of hydriodic acid and is often referred to in the older literature,[43] is not specially to be recommended because even traces of oxygen interfere markedly. Kolthoff *et al.*[44] found that the reduction method with ferrous salt was preferable to others. Previously, Gossart[45] had used the reaction quantitatively, detecting the end-point by spotting with potassium ferricyanide. The method gave only very approximate values and has been further modified in the literature. Szebellédy[46] showed that the formation of the rose-red of the ferrous-nitrogen oxide (NO) complex was a suitable indicator for the titration (p. 609); however, his method cannot be used for exact nitrate determinations. The best results are obtained when the nitrate solution is boiled with excess of ferrous solution under suitable conditions and back-titrated with dichromate. The reaction is then quantitative.

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[39] N. Léontovitch and J Bénard, *Bull. soc. chim. France*, **1946**, **157**.

[40] N. Iritani, *Chem. Abstr.*, **44**, 478 (1950).

[41] H. H. Willard and W. L. Hall, *J. Am. Chem. Soc.*, **44**, 2237 (1922).

[42] J. Gillis and V. Cuvelier, *Naturw. Tijdschr.*, **11**, 20 (1929); cf. V. Cuvelier *ibid.*, 163.

[43] See H. Beckurts, *Die Methoden der Massanalyse*, Vieweg, Braunschweig, 1913.

$$3Fe^{2+} + NO_3^- + 4H^+ \rightarrow 3Fe^{3+} + NO + 2H_2O$$

Even in strong hydrochloric acid media a long time of boiling is necessary for quantitative reaction. However, it has been found that a small amount of molybdate exerts a strong catalytic influence on the reaction rate. Kolthoff, Sandell, and Moskowitz[44] developed a method for nitrate determination which has proved satisfactory. However, it should be remembered that atmospheric oxygen readily oxidizes both the nitrogen oxide formed and the strongly acidic solution of ferrous salt.

Apparatus: A 250 ml. Erlenmeyer flask is fitted with a two-hole rubber stopper. A small dropping funnel (about 3 ml.) with teat is inserted through one hole and filled with the molybdate solution (1 per cent ammonium molybdate tetrahydrate in water). By compression of the teat, the catalyst is readily added to the flask. Through the second entry, a bent glass tube discharges into a bicarbonate solution which has the double advantages that the laboratory is not polluted with strong acid vapors during the boiling and that air cannot enter the flask during the cooling.

Procedure: Place the weighed sample of nitrate (about 0.1–0.2 g.) in the flask and add 25–50 ml. of 0.18*N* ferrous solution in *N* sulfuric acid (it is advisable to use an excess of at least 50 per cent) followed by 70 ml. of 12*N* hydrochloric acid. Add 3–4 g. of sodium bicarbonate carefully in small portions to drive out the air, and immediately stopper the flask. The bent tube discharges through a suspension of 50 g. of sodium bicarbonate in 100 ml. of water. Heat the solution carefully and after boiling for 3 minutes, add the catalyst from the dropper. Continue boiling and after 10 minutes replace the sodium carbonate with a fresh suspension and cool the flask by placing it in cold water. When the solution is cold, add 35 ml. of 6*N* ammonium acetate for every 50 ml. of test solution and 3–5 ml. of 85 per cent phosphoric acid. The acetate depresses the acidity of the solution to 1–2N. Titrate the solution, which should have a volume of about 100–150 ml., slowly with 0.1N dichromate using 6–8 drops of one of the mentioned indicators (Note 1). Standardize the ferrous solution daily under conditions similar to those described above. One milliliter of 0.1N ferrous solution corresponds to 3.370 mg. of KNO_3 or 2.067 mg. of NO_3^-.

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[44] I. M. Kolthoff, E. B. Sandell, and B. Moskowitz, *J. Am. Chem. Soc.*, **55**, 1454 (1933).

[45] Gossart, *Compt. rend.*, 24, 21 (1847).

[46] L. Szebellédy, *Z. anal. Chem.*, **73**, 145 (1928); **74**, 232 (1928).

Notes: (1) An aqueous 1 per cent solution of barium diphenylamine sulfonic acid or diphenylamine or diphenylbenzidine in sulfuric acid solution may be used as indicator. The sodium bicarbonate used should be tested for the absence of nitrite and other oxidizing materials.

(2) The method gives an accuracy of 0.3–0.5 per cent and can be completed in under 20 minutes. Smaller amounts of nitrate can be determined using more dilute solutions of the reagents and keeping the end volume after the boiling to about 50 ml.; then 20 ml. of 6N ammonium acetate, 10 ml. of phosphoric acid, and 25–60 ml. of water are added. Amounts of nitrate from 2–10 mg. can be determined with an accuracy of 2–3 per cent.

(3) Oxidizing materials such as chlorate, bromate, and iodate interfere. However, it is simple to find conditions under which the other oxidants are quantitatively reduced without decomposition of nitrate by ferrous iron.

(4) Small amounts of perchlorate do not interfere, but large amounts cause an overconsumption of ferrous solution. For the determination of 150 mg. of potassium nitrate in the presence of 800 mg. of ammonium perchlorate, the results were 1–1.5 per cent high. Manganous salts and phosphate do not interfere.

Leithe[47] found that the reduction of nitrate by ferrous iron is complete in 3 minutes at boiling temperatures when 65 g. of sulfuric acid per 100 ml. is present. Back-titration of the ferrous iron with dichromate, ferroin (cf. p. 173) being used as indicator, is preferred to the permanganate titration (p. 82).

Reagents: Ferrous sulfate solution (approximately 0.2N): 55 g of pure $FeSO_4 \cdot 7H_2O$ is dissolved in 100 ml. of water containing 1 drop of 50 per cent sulfuric acid and diluted to 1 liter with 50 per cent sulfuric acid (sp. gr. 1.40).

Procedure: Transfer a 25 ml. aliquot of a solution containing 1 g. of the nitrate sample in 500 ml. to a 250 ml. Erlenmeyer flask and add exactly 25 ml. of the ferrous solution with 25 ml. of concentrated sulfuric acid and some small boiling stones. Boil the solution gently for 3 minutes when the color changes from brownish violet to clear yellow. Cool under the tap, add 3–5 ml. of 70–80 per cent phosphoric acid and 50 ml. of water and cool the mixture again until lukewarm. Add 2 drops of 0.025M ferroin solution and titrate the solution with 0.1N dichromate to the end-point from brown to blue-green. Carry out a blank determination in the same way using 25 ml. of water.

Note: This method is suitable for large amounts of nitrate. For 0.03–3 mg. of nitrate, 5 ml. of 0.02N ferrous sulfate solution (prepared in the same way as above), and 5 ml. of concentrated sulfuric acid are used. About 0.2 g. of potassium bicarbonate serves to drive out the air, and then the nitrate sample dissolved in 5 ml. of water is added. The solution is boiled for 3 minutes, 1 ml. of phosphoric acid and 5 ml. of water are added and the solution is cooled and titrated as above, but with 0.01N dichromate solution.

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[47] W. Leithe, *Mikrochemie*, **33**, 48 (1947).

The previously described method is suitable for the determination of even smaller amounts of nitrate if chloride is added and more dilute standard solutions are used; 0.002–0.1 mg. of nitrate can be determined with an accuracy of 0.002 mg., and 0.1–1 mg. with an accuracy of 0.005–0.01 mg. The method is suitable for the determination of nitrate in waters.[48]

Reference has already been made to the procedure of Szabó and Bartha (p. 82), who reduce nitrate with ferrous hydroxide in alkaline medium in the presence of silver ammine sulfate as catalyst. The same authors have described a method for 0.02–0.6 mg. amounts of nitrate based on the same principle;[49] a dichromate titration is used. The following reactions occur:

$$NO_3^- + 2Fe(OH)_2 + H_2O \longrightarrow 2Fe(OH)_3 + NO_2^- \qquad (1)$$

$$NO_2^- + 6Fe(OH)_2 + 5H_2O \longrightarrow 6Fe(OH)_3 + NH_3 + KOH \qquad (2)$$

Reaction (1) proceeds slowly in the absence of silver catalyst unless a high concentration of alkali is present.[50] For an explanation of the mechanism of this catalysis the original paper should be consulted.

Chlorate: Boyle *et al.*[51] reduced chlorate in a fairly strong hydrochloric acid solution with ferrous iron, using ammonium molybdate as a catalyst (cf. p. 81). It is claimed that the following procedure for the analysis of cell liquors is accurate and precise.

Procedure: Pipette a 10 ml. sample of cell liquor into a 500 ml. Erlenmeyer flask, add 2 drops of phenolphthalein indicator, and titrate with 1*N* hydrochloric acid. (An estimation of total alkalinity which is sufficiently accurate for routine purposes may be made at this point.) Add 10 ml. of 0.25*N* ferrous ammonium sulfate solution, 3 drops of 10 per cent ammonium molybdate catalyst, and 40 ml. of concentrated hydrochloric acid. Allow the mixture to stand for 1 minute for complete reaction, and then add 20 ml. of phosphoric acid–sodium acetate buffer reagent (250 ml. of concentrated phosphoric acid plus 1 liter of 4*M* sodium acetate). Dilute to 200 ml. with distilled water, add 3 drops of 0.3 per cent diphenylaminesulfonate indicator, and titrate with 0.1*N* potassium dichromate to the purple end-point. A correction of 0.05 ml. of dichromate is made for each 6 drops of indicator solution.

Williams[52] has determined chlorate in caustic soda by a similar process but uses a sulfuric acid medium. The molybdate catalyst is not added.

Procedure: Take a 5 g. sample of 50 per cent caustic soda for analysis and dilute with 25 ml. of water. Add 20–25 ml. of 1:1 phosphoric acid and swirl to mix. Add 10 ml. of 0.1*N* ferrous sulfate and 45–50 ml. of 12*N* sulfuric acid. Allow to stand for 10 minutes or longer. Add approximately 0.5 ml. of 0.01*M* diphenylaminesulfonic acid and titrate the excess ferrous sulfate with 0.1*N* potassium dichromate solution. The end-point should be taken when the maximum purple color develops.

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[48] W. Leithe, *Mikrochemie*, **33**, 149 (1947).

[49] Z. G. Szabó and L. Bartha, *Mikrochemie*, **38**, 413 (1951).

[50] Z. G. Szabó and L. Bartha, *Acta Chim. Acad. Sci. Hung.*, **1**, 116 (1951).

[51] A. J. Boyle, V. V. Hughey, and C. C. Casto, *Ind. Eng. Chem., Anal. Ed.*, **16**, 370 (1944).

[52] D. Williams, *Ind. Eng. Chem., Anal. Ed.*, **17**, 533 (1945).

Note: Normally 10 ml. of 0.1*N* ferrous sulfate is sufficient to complete the reduction in 10 minutes. However, if less than 5 ml. of potassium dichromate is required for the titration, the analysis must be repeated using a larger amount of ferrous sulfate.

Organic Peroxides: Organic peroxides in gas oils can be determined by reacting with a standard solution of Mohr's salt and titrating the excess with standard dichromate. The material is dissolved in glacial acetic acid before the ferrous solution is added.[53] The method gives results of only fair accuracy because of an abundance of induced reactions. In the absence of oxygen the reaction ratio of ferrous to peroxide is much less than 2 because of induced decomposition of the peroxide. This can often be greatly diminished by the addition of much acetone and (or) of bromide. In the presence of oxygen the reaction ratio of iron to peroxide is much greater than 2 because of the induced air-oxidation of ferrous iron.[54] Instead of using a one-electron donor like ferrous iron, much better results can be obtained with a two-electron donor like stannous tin or arsenious oxide. Barnard and Hargrave[55] used stannous tin as reductant; its use also avoided interference from sulfur present in the peroxides which were examined. After the reduction, the excess of stannous tin is oxidized with ferric iron and the ferrous iron so formed is titrated with dichromate (cf. p. 620).

Procedure: Dissolve the sample (0.75–1 meq.) in 10 ml. of glacial acetic acid in a 250 ml. Erlenmeyer flask. Evacuate to 20 mm. of mercury. Pipette in 15 ml. of 0.1*N* stannous chloride (Note 1), reevacuate the flask, and fill it with nitrogen. Repeat the evacuation twice. Set aside for 1 hour at room temperature and then add a boiling solution of 5 ml. of ferric solution (200 g. of ferric alum in 1 liter of water containing 60 ml. of concentrated sulfuric acid), 1 g. of ammonium chloride, and 45 ml. of water. Heat at 75°C. for 30 seconds, cool rapidly, add 10 ml. of a solution containing 75 ml. of phosphoric acid and 75 ml. of sulfuric acid in 350 ml. of water, and titrate with 0.05*N* potassium dichromate. Use 6 drops of 0.25 per cent aqueous diphenylaminesulfonic acid solution as indicator.

Notes: (1) The 0.1*N* stannous chloride is prepared by dissolving 11.3 g. of the dihydrate in 75 ml. of hydrochloric acid (density 1.18) and 925 ml. of oxygen-free water. This is stored under nitrogen and is dispensed by means of a pipette passing through the stopper, which is filled by increasing the nitrogen pressure.

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[53] E. M. Tanner and T. F. Brown, *J. Inst. Petroleum*, **32**, 341 (1946).

[54] I. M. Kolthoff and A. I. Medalia, *Anal. Chem.*, **23**, 595 (1951).

[55] D. Barnard and K. R. Hargrave, *Anal. Chim. Acta.*, **5**, 476 (1951); earlier literature is given in this paper.

(2) The method is not suitable for dialkyl peroxides. Aldehydes, thioethers, and considerable amounts of primary alcohols interfere.

Determination of Metals after Reduction. Ferric Iron: For general methods of reduction see pp. 9–23.

Stannous Chloride Method: The stannous chloride method is generally used in conjunction with a dichromate titration. For details of the reduction see p. 84. The titration of ferrous iron is then done with dichromate and a suitable indicator in place of permanganate. Reinhardt-Zimmermann preventive solution need not be added of course.

To avoid the possibility of adding an undue excess of stannous chloride, Titus and Sill[56] reduce in the presence of silicomolybdic acid which gives a blue color when excess of stannous tin is added. Wehber[57] uses cacotheline as indicator to detect the excess of stannous tin by the appearance of a violet color. Dichromate is then added carefully until the color changes to yellow or greenish yellow, and finally the iron is titrated with dichromate using sodium diphenylaminesulfonate as indicator. The authors suggest the use of cacotheline as indicator and the removal of the slight excess of tin(II) with mercuric chloride.

Sulfurous Acid Method: The reducing action of sulfurous acid on ferric salts has not been fully studied. Some authorities indicate that the reaction proceeds best in a neutral solution, being incomplete in a sulfuric acid or a hydrochloric acid medium. Others consider that a slightly acid medium gives the best results. The amount of iron, it is claimed, must not be too great.

The equation for the reaction is usually stated to be as follows:

$$Fe_2(SO_4)_3 + SO_2 + H_2O \longrightarrow 2FeSO_4 + H_2SO_4$$

The mechanism of the reduction, however, is undoubtedly more complicated than this equation suggests. A red compound is first formed which appears to be a salt of ferrisulfurous acid, with the possible formula $Fe(Fe(SO_3)_3)$. This breaks down thus:

$$Fe(Fe(SO_3)_3) \longrightarrow FeS_2O_6 + FeSO_3$$

and hydrolysis then produces ferrous sulfate and sulfurous acid:

$$FeS_2O_6 + H_2O \longrightarrow FeSO_4 + H_2SO$$

Burriel and Lucena[58] studied the mechanism of the reduction and found that the reaction was accelerated and that a higher acidity could be tolerated when thiocyanate was present. The mechanism of the reaction was suggested to be the partial replacement of sulfite by thiocyanate in the intermediate compound, $Fe(Fe(SO_3)_3)$.

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[56] A. C. Titus and C. W. Sill, *Ind. Eng. Chem., Anal. Ed.*, **13**, 416 (1941).

[57] P. Wehber, *Angew. Chem.*, **66**, 271 (1954).

[58] F. M. Burriel and F. C. Lucena, *Anal. Chim. Acta*, **3**, 547 (1949); cf. idem, *Inform. quim. anal. (Madrid)*, **4**, 81 (1950).

The thiocyanate-accelerated reaction has possible applications in determinations where it is inconvenient to work in a neutral solution because of hydrolysis of other components such as titanium. At an acidity of 1.0–1.5N in sulfuric acid, titanium is not precipitated, even after prolonged boiling.

Satisfactory results are obtained when determination of iron(III) is carried out in the presence of appreciable quantities of titanium.

Procedure: Add 10 ml. of 0.1N potassium thiocyanate solution to the solution of iron(III), which should be less than 2N in sulfuric acid. Saturate the solution with sulfur dioxide in the cold, or add 50 ml. sulfurous acid solution. Heat slowly to boiling. The solution rapidly becomes colorless or only slightly yellow, and the reduction is then complete. Pass carbon dioxide until all the sulfur dioxide has been removed, cool the solution, and add 10 ml. of 0.1M mercuric nitrate or mercuric sulfate solution.

Titrate in the usual way using potassium dichromate solution or potassium permanganate solution, with barium diphenylamine sulfonate as indicator.

Other Reduction Methods: Henry and Gelbach[59] reduce the ferric solution in 1N hydrochloric acid through the silver reductor and titrate with standard dichromate solution using diphenylaminesulfonic acid as indicator. Manganese, chromium, and titanium do not interfere. Vanadium does not interfere in concentrations of 100 mg. or less in 200 ml. of titrating solution.

Cooke, Hazel, and McNabb[60] showed that in the reduction of ferric iron with liquid zinc amalgam the addition of a little chromous chloride has a favorable effect. Chromous chloride reduces phenosafranine to a colorless product. Upon shaking with air, the chromous chromium is oxidized and the indicator turns pink before ferrous iron is oxidized. The latter then can be titrated.

The reduction can also be carried out with chromous chloride without zinc amalgam when the amount of ferric iron is between 0.1 and 10 mg. in 25 ml.[61]

Procedure: Add to 25 ml. of the ferric iron solution containing free hydrochloric or sulfuric acid 2 to 3 drops of 0.01 per cent phenosafranine solution and add dropwise chromous chloride solution until the pink color changes into a light clear green. Swirl until the pink color reappears, add a few drops 50 per cent phosphoric acid and diphenylaminesulfonate indicator, and titrate with 0.003–0.007*N* standard dichromate solution until a purple color appears. Apply an indicator correction.

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[59] J. L. Henry and R. W. Gelbach, *Ind. Eng. Chem., Anal. Ed.*, **16**, 49 (1944); cf. F. M. Burriel and F. Pino Pérez, *Anales real soc. españ. fis. y quím.* (*Madrid*), **47B**, 305 (1951); J. L. P. Wyndham, *S. African Ind. Chem.*, **5**, 73 (1951).

[60] W. D. Cooke, F. Hazel, and W. M. McNabb, *Anal. Chem.*, **21**, 643 (1949).

[61] W. D. Cooke *et al.*, *ibid.*, **21**, 1011 (1949).

Aluminium powder,[62] zinc pellets,[63] and nickel[64] have also been recommended for use in conjunction with the dichromate titration.

Uranium: Lundell and Knowles[65] have shown that the reduction of hexavalent uranium with the zinc reductor leads to a mixture of U(III) and U(IV). The trivalent uranium is rapidly oxidized by air to the tetravalent state. This has been confirmed, and it has also been found that the tetravalent uranium is fairly stable to air.[66] Kolthoff and Lingane[67] reduced uranyl salts to trivalent uranium with the Jones reductor, oxidized to tetravalent uranium in an air stream, and titrated with dichromate, diphenylaminesulfonic acid or diphenylamine being used as indicator.. The color change occurs very slowly but, when an excess of ferric chloride is added, uranium(IV) rapidly reduces it to an equivalent amount of ferrous:

$$U^{4+} + 2Fe^{3+} \rightleftharpoons U^{6+} + 2Fe^{2+}$$

which can then be titrated in the usual way.

Procedure: Dilute the solution to 100 ml. and acidify with 5 ml. of concentrated sulfuric acid. Cool to room temperature. Wash the Jones reductor (amalgamated zinc with 2–3 per cent of mercury; a layer of about 20 ml.) with 50 ml. of 1:20 sulfuric acid and then pass the test solution through at a speed of 50 ml. per minute. Collect the effluent in a filter flask and wash the zinc with 30 ml. of 1:20 sulfuric acid and twice with water. The reduced solution is olive green. Pass pure air through the solution for 5–10 minutes to oxidize the U(III) to U(IV). Then add 25 ml. of 2 per cent ferric chloride (0.12*N*), 15 ml. of 85 per cent phosphoric acid, and 10 drops of 0.2 per cent barium diphenylaminesulfonate or diphenylamine and titrate the solution fairly slowly with dichromate.

Notes: (1) The results are accurate to 0.2 per cent. Very dilute solutions can also can be titrated accurately.

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[62] Cf. E. R. Riegel and R. D. Schwartz, *Anal. Chem.*, **24**, 1803 (1952).

[63] G. Norwitz, *Metallurgia*, **43**, 154 (1951) (aluminium alloys).

[64] A. C. Simon, P. S. Miller, J. C. Edwards, and F. B. Clardy, *Anal. Chem.*, **18**, 496 (1946) (bronze and copper alloys).

[65] G. E. F. Lundell and H. B. Knowles, *J. Am. Chem. Soc.*, **47**, 2637 (1925).

[66] N. H. Furman and I. C. Schoonover, *J. Am. Chem. Soc.*, **53**, 2561 (1931).

[67] I. M. Kolthoff and J. J. Lingane, *ibid.*, **55**, 1871 (1933).

(2) Schreyer and Baes[68] applied the above method in the presence of phosphate. By adjustment to an optimum acidity of 4.5*M* in sulfuric acid, precipitation of uranium(IV) phosphate in the reductor is avoided. Under these conditions the aeration procedure is unnecessary, for only uranium(IV) is formed. When nitrate is present, it can be removed by fuming the solution with sulfuric acid in order to avoid the formation of hydroxylamine in the Jones reductor.

Cooke, Hazel, and McNabb[69] recommend the use of a lead reductor (p. 16). In sulfuric acid solution an adherent film of lead sulfate is formed, but in the presence of hydrochloric acid (greater than 2.5*M*) this film formation is prevented.

Procedure: To 50 ml. of solution of acidity 0–9*N* in sulfuric acid and containing 40–200 mg. of uranium add sufficient hydrochloric acid to give a concentration of 3*N*. Pour the solution through the reductor and allow it to flow into 10 ml. of 5 per cent ferric sulfate solution. Wash the column with five to six 25 ml. portions of 1 : 15 hydrochloric acid. Add to the solution 10 ml. of 85 per cent phosphoric acid and titrate with 0.05*N* dichromate. Add 0.5 ml. of 0.3 per cent diphenylaminesulfonic acid indicator near the endpoint. Deduct an indicator blank of 0.10 ml. of 0.05*N* dichromate.

Notes: (1) The column used was 25 cm. long and 2 cm. in diameter. When not in use the lead was covered with 1*N* hydrochloric acid containing about 1 per cent ferric iron. Without this addition the first result was always low. Before use, wash with six 25 ml. portions of 1: 15 hydrochloric acid.

(2) 5,6-Dimethylphenanthroline is also recommended as indicator; the indicator correction is smaller.

Main[70] reduces with stannous chloride; he remarks that the reduction is unsatisfactory unless a catalyst is used and claims that there are some advantages to his procedure. The reduction is stayed at the uranium(IV) stage, nitrate does not interfere, and there is no poisoning of the reducing agent (as occurs with the Jones reductor) when phosphate, arsenate, or bismuthate is present.

Procedure: To 10 ml. of uranyl sulfate solution pipette in 2 ml. of 0.02*N* ferric chloride catalyst (0.5585 g. of iron wire dissolved in 20 ml. of concentrated hydrochloric acid, then oxidized with a few drops of hydrogen peroxide and diluted to 500 ml.), 20–25 ml. of concentrated hydrochloric acid and 4 ml. of 1:1 phosphoric acid. Cover and heat to 96–99°C. Add an excess of stannous chloride solution (5 per cent of the dihydrate in 1 : 10 hydrochloric acid) and heat for 10–15 minutes. Cool, decompose the excess of stannous ion with 20 ml. of saturated mercuric chloride solution, and add 20 ml. of 8 per cent ferric chloride solution. Dilute to 250–300 ml. and titrate with 0.02*N* potassium dichromate using 0.25 ml. of 0.005*M* diphenylaminesulfonic acid as indicator. Run a blank on the same amount of ferric chloride catalyst solution.

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[68] J. M. Schreyer and C. F. Baes, *Anal. Chem.*, 25, 644 (1953).

[69] W. D. Cooke, F. Hazel, and W. M. McNabb, *Anal. Chem.*, 22, 654 (1950).

[70] A. R. Main, *Anal. Chem.*, 26, 1507 (1954).

Notes: (1) The titration is accurate to 0.5 per cent.

(2) Arsenic, perchlorate, tungstate, permanganate, ammonium ions, pyridine, bismuthate, cobalt(II), sulfate, chloride, and less than 5 mg. of nitrate do not interfere. Molybdenum(VI), copper(II), titanium(IV), and vanadate cause high results.

(3) Small amounts of uranium(VI) may be determined by reduction with chromous chloride,[71] the excess being destroyed by atmospheric oxidation. Phenosafranine is used as indicator to enable the process to be followed (cf. p. 188). Ferric sulfate is then added and the titration is completed in the usual way.

(4) Rao, Murty, and Rao[72] consider that the objections which have been raised to the direct titration of uranium(IV) with dichromate are due to the particular indicators which have been used. When *N*-phenylanthranilic acid is used, satisfactory end-points are obtained. Contrary to most other investigators, they state that the reaction between dichromate and uranium(IV) is sufficiently rapid for titrations to be done at room temperatures. The speed of oxidation of the indicator increases with acid concentration but is retarded in the presence of uranium(VI). However, the presence of uranium(IV) markedly accelerates the oxidation. This general effect is attributed to the faster reaction between dichromate and uranium(IV) inducing the slower reaction between dichromate and indicator.

Procedure: To 10–25 ml. of approximately $0.05N$ uranium(IV) solution add 50 ml. of $10N$ sulfuric acid and dilute to 100 ml. Add 2 drops of 0.1 per cent *N*-phenylanthranilic acid and titrate with $0.05N$ dichromate until a pink color is obtained.

Sodium: The method for uranium was applied by Kolthoff and Lingane[67] to the semimicro determination of sodium. A concentrated solution of zinc uranyl acetate is a specific reagent for sodium under the correct conditions. The triple salt formed, which is insoluble in the reagent but soluble in water, has the formula $(UO_2)_3$-$ZnNa(CH_3COO)_9 \cdot 6H_2O$. Thus only 1 mg. of sodium gives 66.88 mg. of the triple salt and the reaction is to be recommended for the gravimetric determination of sodium. For the determination of traces of sodium, the following titrimetric method is advantageous. It is based on the precipitation method of Barber and Kolthoff.[73]

Reagent Solution: (A) 10 g. of uranyl acetate dihydrate, 6 g. of 30 per cent acetic acid, and 50 g. of water. (B) 30 g. of zinc acetate trihydrate, 3 g. of 30 per cent acetic acid, and 50 g. of water. After the salts in solutions A and B have been dissolved by warming, the solutions are mixed and after 24 hours the sodium zinc uranyl acetate which has separated is filtered off. The reagent is indefinitely stable when kept in Jena or Pyrex glass.

Procedure: Evaporate the test solution containing less than 12 mg. of sodium to dryness on the water bath. Treat the residue with 15 ml. of reagent, mix and stir well, especially for the first 10 minutes. After 1 hour, filter the precipitate on a glass filter crucible (G4), or a micro crucible for very small amounts, and remove as much as possible of the liquid by suction. Wash the precipitate with five to ten 2 ml. portions of the reagent and then with five 1–2 ml. portions of 95 per cent ethanol which has been previously saturated with the precipitate. Dissolve the precipitate in 5 per cent sulfuric acid and determine the uranium content as given on p. 189.

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[71] W. D. Cooke, F. Hazel, and W. M. McNabb, *Anal. Chim. Acta*, 3, 656 (1949).

[72] V. P. Rao, B. V. S. R. Murty, and G. G. Rao, *Z. anal. Chem.*, 147, 99 (1955).

[73] H. H. Barber and I. M. Kolthoff, *J. Am. Chem. Soc.*, 50, 1625 (1928).

One milliliter of $0.1N$ dichromate corresponds to 0.382 mg. of sodium.

Notes: (1) The method requires little time. Six precipitates can be titrated in less than half an hour.

(2) The results are accurate to 1 per cent for more than 0.3 mg. of sodium. Even 0.07–0.1 mg. can be determined with an accuracy of 3–5 per cent. The absolute error in such a micro determination is thus very small.

(3) Potassium does not interfere when less than 10 mg. is present. When more than 1 mg. of sodium is present, even 25 mg. of potassium can be tolerated. Small amounts of ammonium, cesium, rubidium, alkaline earths, manganese, lead, aluminium, cadmium, etc., do not interfere. If large amounts are present, a reprecipitation is necessary. The method can be used for the determination of traces of sodium in salts of these metals.

Phosphate and arsenate are previously removed with magnesia mixture which must be free from sodium. Large amounts of ferric iron and aluminium are removed with sodium-free ammonia. For further details, the original paper should be consulted.

Tungsten: Vlasak[74] used lead amalgam and the reduction apparatus of Someya for the conversion of tungsten(VI) to tungsten(III).

Procedure: Evaporate the tungstate solution until the salt separates, and dissolve in the least possible water. Add 50–100 ml. of concentrated hydrochloric acid (sp. gr. 1.19) and reduce the solution in the Someya apparatus (p. 20) at 50°C. with 20 ml. of lead amalgam, after the air has been removed with carbon dioxide. Shake the solution strongly during the reduction and if necessary warm until the color changes from yellow to greenish yellow when the reduction to tungsten(III) is complete. Titrate in the absence of air with potassium dichromate. When the solution turns green (tungsten(V)), add 2 drops of 1 per cent diphenylamine solution and complete the titration dropwise to the change to blue-violet.

Notes: (1) The accuracy is about 0.2 per cent. The titration may also be done with potassium bromate or cupric sulfate.

(2) Holt and Gray[75] obtained excellent results by a similar method for the determination of macro and semimicro quantities of tungstate. The procedure was applied to the determination of tungsten in tungsten-nickel alloys and ferrotungsten.

Other Determinations. ***Tellurium:*** The oxidation of tellurous acid by dichromate was studied by Lenher and Wakefield.[76] Oxidation proceeds slowly in acid solution; hydrochloric acid reacts

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[74] F. Vlasak, *Coll. Czech. Chem. Commun.*, 10, 278 (1938).

[75] M. L. Holt and A. G. Gray, *Ind. Eng. Chem., Anal. Ed.*, 12, 144 (1940).

[76] V. Lenher and H. F. Wakefield, *J. Am. Chem. Soc.*, 45, 1423 (1923). A review of methods for determination of selenium and tellurium is given by V. Lenher, *Proc. Am. Phil. Soc.*, 65, 33 (1926).

$$3TeO_2 + K_2Cr_2O_7 + 8HCl \longrightarrow 3H_2TeO_4 + 2KCl + 2CrCl_3 + H_2O$$

slowly with telluric acid to yield free chlorine especially at higher temperatures; hence the conditions must be controlled carefully.

Procedure: Dissolve the sample (0.1–0.3 g. of tellurium) in 10 ml. of concentrated hydrochloric acid and dilute to 200 ml. with water. Add an excess (1–5 ml.) of $0.1N$ potassium dichromate and set aside for 30 minutes. Add excess of $0.1N$ ferrous sulfate solution and titrate with $0.1N$ dichromate using the external indicator method with potassium ferricyanide solution to detect the end-point.

Notes: (1) The solution should contain only about 2 per cent of free hydrochloric acid.

(2) Willis[77] makes use of the method for the determination of traces (about 1 p.p.m.) of tellurium in copper. Dissolve 10–25 g. of sample in a flask by adding slowly 50–100 ml. of concentrated nitric acid and heating. When red fumes appear, dilute the solution to 200 ml. and add sodium hydroxide until all the acid is neutralized. Redissolve any cupric oxide which has separated by careful addition of nitric acid. Add 4 per cent sodium carbonate solution until a slight precipitate forms and then add 20 ml. more. Boil for 20 minutes, cool thoroughly, and filter, the precipitate being washed with cold water. Dissolve the precipitate, which holds all the tellurium and selenium, back into the flask with 15 ml. of hydrochloric acid and wash the filter paper with water. Boil the solution, keep hot for 5 minutes, dilute to 150 ml., and cool; titrate the tellurium by the procedure of Lenher and Wakefield, but after adding a measured excess of standard ferrous sulfate, complete the titration with dichromate using diphenylamine or its sulfonic acid as indicator.

There appears to be no reason why an internal indicator should not also be used in the older procedure.

(3) Moser and Miksch[78] preferred to oxidize in neutral solution to avoid oxidation of hydrochloric acid. They neutralized with sodium hydroxide solution, and warmed on a steam bath for 10 minutes after adding a slight excess of $0.1N$ dichromate solution. They titrated with a standard solution of Mohr's salt using the external indicator method.

(4) Kruse *et al.*[79] have described a method for the determination of tellurium in organic compounds where somewhat vigorous conditions are required for the decomposition. The sample is digested initially with concentrated nitric acid, and decomposition is completed by the addition of perchloric acid.

Procedure: Weigh the sample (0.075–0.25 g. of tellurium) into a 400 ml. beaker, add 10 ml. of concentrated nitric acid, and warm until the sample dissolves and a pale-colored solution is obtained. Avoid taking the solution to dryness. Cool, add 10 ml. of 1:1 nitric acid and 10 ml. of 70 per cent perchloric acid, heat carefully under a hood until fumes of perchloric acid appear and a colorless solution is obtained. The volume should be less than 10 ml. and the solution should be water-white. Cool, dilute to 200 ml., and add sufficient $0.1N$ dichromate to give an excess of at least 5 ml. Stir and set aside for at least 30 minutes. Add an excess of a $0.1N$ solution of Mohr's salt and add phosphoric acid and sodium diphenylamine sulfonate indicator. Titrate with $0.1N$ dichromate.

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[77] U. F. Willis, *Analyst*, **66**, 415 (1941).

[78] L. Moser and R. Miksch, *Monatsh.*, **44**, 351 (1923).

[79] F. H. Kruse, R. W. Sanftner, and J. F. Suttle, *Anal. Chem.*, **25**, 500 (1953).

Lang and Faude[80] established that telluric acid does not oxidize hydrochloric acid, but that the reason for the formation of chlorine is to be found in the induced oxidation of chloride by the system chromic acid–tellurous acid; the chlorine development can be prevented by Mn(II) or Ce(III) salts according to the principle of acceptor displacement. Thus Mn(II) or Ce(III) is liable to induced oxidation to an extent that is given by the maximum induction ratio 0.5. This number, which indicates that for 1 equivalent of tellurous acid, $^1/_2$ equivalent of acceptor is cooxidized, shows that the oxidation of tellurous acid with dichromate in the presence of Mn(II) or Ce(III) salts proceeds according to the following scheme:

$$Cr^{6+} + Te^{4+} \longrightarrow Cr^{4+} + Te^{6+}$$

$$Cr^{4+} + Mn^{2+} \longrightarrow Cr^{3+} + Mn^{3+}$$

or

$$Cr^{4+} + Ce^{3+} \longrightarrow Cr^{3+} + Ce^{4+}$$

Lange and Faude[80] allowed the reaction between excess of dichromate in a concentration of 10–15 volume per cent sulfuric acid (which must be present in addition to the hydrochloric acid) and tellurous acid to proceed for 15 minutes in the presence of manganous sulfate or cerous nitrate. The excess of dichromate is titrated with ferrous sulfate. The basis for the calculation is the overall equation:

$$2Cr^{6+} + 3Te^{4+} \longrightarrow 2Cr^{3+} + 3Te^{6+}$$

For the purpose of measuring the excess of dichromate, it should be noted that, with the induction ratio 0.5, for the oxidation of a equivalents of tellurous acid, $a + 0.5a = 1.5a$ equivalents of dichromate are required.

Procedure: (for up to 64 mg. of tellurium): Treat the tellurite solution, which may contain up to 20 ml. of concentrated hydrochloric acid, with 10–15 ml. of concentrated sulfuric acid and a solution of 3 g. of manganous sulfate in water. Dilute the solution to 100 ml. with water, cool to room temperature, and pipette in 25 ml. of 0.1*N* dichromate solution. After 15 minutes titrate the solution with 0.1*N* ferrous sulfate using 2 drops of 0.01*N* ferroin (p. 127) as indicator. The color change is sharp from yellow-green to brown.

For amounts of tellurium up to 160 mg., use 15 ml. of concentrated sulfuric acid and 50 ml. of 0.1*N* dichromate; otherwise the method is as given.

Notes: (1) The procedure is accurate to about 0.2 per cent.

(2) Instead of ferroin, *N*-phenylanthranilic acid (p. 175) can be used as indicator.

(3) Lang and Faude also give a procedure for the titration of tellurite in presence of bromide. This is of practical importance because in a mixture of As(III), Sb(III), and Te(IV) the sum of As(III) and Sb(III) can be determined with

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[80] R. Lange and E. Faude, *Z. anal. Chem.*, 108, 258 (1937).

bromate and then Te(IV) can be determined in the titrated solution. Various methods for the determination of the first two ions in presence of Te(IV) can be found in the original paper.

(4) Selenious acid does not interfere in the titration of tellurium.

Sulfite: The determination of sulfite by titration with various oxidimetric reagents has been studied by a large number of investigators; in general it has been concluded that the errors are due to the formation of dithionate.

Bonner and Yost[81] studied the errors of a number of methods. They state that the error with dichromate is about 3 per cent. According to Rao and Rao,[82] the oxidation of sulfite by various oxidants can be made to proceed quantitatively when suitable catalysts are used. In a hydrochloric acid medium good results are obtained by oxidation with dichromate without a catalyst, provided that the acid concentration is maintained between 0.5 and 1.0*N;* at higher concentrations, catalysts (copper sulfate or iodine monochloride) are necessary. In sulfuric acid medium a catalyst (iodine monochloride) is necessary at all concentrations (0.1–5.0*N*). When an acetic acid medium is used, the reaction is quantitative without the addition of a catalyst.

Procedure: Run 10–15 ml. of the sulfite solution (0.05*N*) into a known excess (10–15 ml.) of 0.05*N* potassium dichromate containing sufficient acetic acid to give a final acid concentration of 1–3 *N* or sufficient hydrochloric acid to give a final acid concentration of 0.5–1*N*. After 1 minute, titrate the excess of dichromate with a solution of 0.05*N* Mohr's salt in the presence of *N*-phenylanthranilic acid or diphenylbenzidine indicator.

Note: Good results were obtained when the amount of sulfite was less than 1 millimole. At 1 millimole and higher the error appears to increase suddenly to about 0.5–0.6 per cent under all conditions.

Dithionate: Dithionate is quantitatively oxidized to sulfate by boiling in acid solution with excess of dichromate:

$$Cr_2O_7^{2-} + 3S_2O_6^{2-} + 2H^+ \longrightarrow 2Cr^{3+} + 6SO_4^{2-} + H_2O$$

Procedure:[83] To 25 ml. of approximately 0.0125*M* dithionate solution, add 10 ml. of 0.15*N* potassium dichromate and 10 ml. of about 10*N* sulfuric acid. Boil the mixture for 1 hour, replacing the water occasionally as it evaporates. Cool and titrate the excess of dichromate iodometrically.

Note: Any sulfurous acid present can previously be boiled out from 0.5*N* acetic acid solution; dithionate is not then attacked.

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[81] W. D. Bonner and D. M. Yost, *Ind. Eng. Chem.*, 18, 55 (1926).

[82] K. B. Rao and G. G. Rao, *Anal. Chim. Acta*, 13, 313 (1955). (These authors also review the findings of many of the earlier investigators.)

[83] S. Glasstone and A. Hickling, *J. Chem. Soc.*, 1933, 5.

Tin (II) may be determined by direct titration with standard dichromate in an inert atmosphere. For example, Saz[84] determined tin in cassiterite in this way. He reduced with zinc and sodium hydroxide, acidified and added sodium bicarbonate. Diphenylamine was used as indicator.

Under suitable conditions, the lower oxidation states of *rhenium* can be oxidized by acid or alkaline dichromate solutions to rhenium(VIII). The excess of dichromate is determined by the addition of excess ferrous sulfate and back-titration with permanganate or ceric sulfate.[85]

Burriel and Sierra[86] titrated $0.025M$ *ferrocyanide* solution with $0.02N$ dichromate in about $0.3N$ hydrochloric acid medium using benzidine acetate as indicator. *Zinc* can be determined by precipitation as zinc ferrocyanide if the excess of ferrocyanide in the filtrate is titrated.

Someya[87] determined *titanium* salts by reducing with bismuth amalgam in hydrochloric acid solution to titanium(III) and then titrating with dichromate solution.

Columbic acid (Cb_2O_5) is quantitatively reduced to Cb_2O_3 in the Someya reductor with zinc amalgam.[88] This is then decomposed by excess of ferric chloride, and the latter is titrated with titanous chloride in a stream of carbon dioxide using thiocyanate as indicator.

$$Cb_2O_3 + 4FeCl_3 + 2H_2O \longrightarrow Cb_2O_5 + 4FeCl_2 + 4HCl$$

It would probably be much easier to titrate the ferrous iron formed from the ferric chloride directly with potassium dichromate or ceric sulfate.

Precipitated arsenic which is obtained by the reduction of arsenite with hypophosphite can be filtered off and determined by oxidation with standard potassium dichromate solution in strong sulfuric acid medium. The excess of dichromate is determined by titration with ferrous sulfate.[89]

Antimony(III) may be determined by oxidation with dichromate.[90] It is necessary to allow the oxidation to proceed for 2–3 hours and the end-point is not very sharp. The method appears to be unattractive. *Arsenic(III)* is similarly oxidized to the pentavalent state.

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[84] E. Saz, *Chem. Zentr.*, 1926, I, 2725.

[85] W. Geilmann and F. W. Wrigge, *Z. anorg. Chem.*, 222, 56 (1935).

[86] F. Burriel-Marti and F. Sierra, *Anales soc. españ. fís. y quím. (Madrid)*, 32, 87 (1934).

[87] K. Someya, *Science Repts. Tohôku Imp. Univ.*, 15, 400 (1926); cf. *Z. anorg. Chem.*, 152, 380 (1926).

[88] V. Schwarz, *Z. angew. Chem.*, 46, 552 (1933). See also J. A. Tschernikov and M. P. Karssajevskaya, *Z. anal. Chem.*, 99, 398 (1934).

[89] W. J. Agnew, *Analyst*, 68, 171 (1943).

[90] J. Knop, *Z. anal. Chem.*, 63, 96 (1923).

Selenium may be determined in the presence of tellurium; iodine monochloride is used as catalyst and *N*-phenylanthranilic acid as indicator.[91]

The original papers should be consulted for details.

3. Methods for Organic Compounds. ***Hydroquinone:*** Kolthoff[92] found that hydroquinone could be titrated directly with dichromate solution at 40–60°C.

$$C_6H_4O_2H_2 + O \rightleftharpoons C_6H_4O_2 + H_2O$$

Procedure: To 25 ml. of hydroquinone solution, add 15–20 ml. of 4*N* hydrochloric or sulfuric acid, 3 drops of 0.1 per cent diphenylamine indicator, warm to 40–60°C. and titrate with 0.1*N* dichromate. At the beginning of the titration, the solution is yellow because of the quinone formed; toward the end, it changes to a dirty green (mixture of chromic salts and quinone). Near the end-point add the dichromate very slowly and allow 10 seconds between drops.

Notes: (1) Under the conditions given, the titration is accurate to 0.2 per cent. Even with 0.01*N* solutions the results are wholly satisfactory; in this case, the titration must be done very slowly near the end-point; otherwise the consumption of dichromate will be too high.

(2) Phenol and cresol do not interfere; hence the method is suitable in many cases where the iodometric method fails.

Indirect Oxidations with Dichromate: Many organic compounds are oxidized completely to carbon dioxide and water by dichromate in strong acid solution. The excess can be titrated iodometrically or with ferrous solution in the presence of phosphoric acid and diphenylamine.

Methanol is thus quantitatively oxidized; ethanol goes only to acetic acid and water. Reischauer[93] based a determination of alcohols on this method, which was later used by many authors.[94] Cardone and Compton[95] determined ethylene glycol by oxidation with dichromate in various concentrations of sulfuric acid; the oxidation numbers varied with the acid concentration. Glycerin is also completely oxidized to carbon dioxide and water, eight oxygens being required.[96] Lactic acid is also oxidized.[97] A method for the quantitative determination of tartaric acid has also been developed.[98]

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[91] V. S. Syrokomskiĭ and R. N. Knyazeva, *Zavodskaya Lab.*, 15, 1149 (1949).

[92] I. M. Kolthoff, *Rev. trav. chim.*, 45, 745 (1926).

[93] Reischauer, *Dingler's Polytech. J.*, 165, 451 (1862).

[94] O. Hehner, *Analyst*, 12, 44, 65 (1887); A. H. Allen and W. Chattaway, *ibid.*, 16, 102 (1891); F. G. Benedict and R. S. Norris, *J. Am. Chem. Soc.*, 20, 293 (1898); M. Cotte, *Z. anal. Chem.*, 40, 417 (1901); E. Martin, *Moniteur Scient.*, (4) 17, 570 (1903); O. Blank and H. Finkenbeiner, *Ber.*, 39, 1326 (1906).

[95] M. J. Cardone and J. W. Compton, *Anal. Chem.*, 25, 1869 (1953); cf. 24, 1903 (1952).

[96] O. Hehner, *Analyst*, 12, 41 (1887); *J. Soc. Chem. Ind.*, 8, 44 (1889).

[97] K. Hansen, *Biochem. Z.*, 167, 58 (1926).

Often the oxidation of the organic compound is incomplete and complications arise because of the formation of carbon monoxide and other side products. A complete investigation of this subject has been carried out by Simon,[99] who suggested the great improvement of silver dichromate; silver catalyzes the oxidation.

For the determination of benzoic acid, mannitol, saccharose, malonic acid, methanol, succinic acid, glutaric acid, and adipic acid, Snethlage[100] found that the oxidation with dichromate was better in 80 per cent sulfuric acid.

Schulz[101] determined starch and starch derivatives, laurylamine acetate, and sodium oleate by oxidizing with dichromate in an autoclave.

[98] K. Täufel and C. Wagner, *Z. anal. Chem.*, **67**, 16 (1925).

[99] L. J. Simon and coworkers, *Compt. rend.*, **170**, 154, 734 (1920); **174**, 1706 (1922); **175**, 167, 525, 768, 1070 (1922); **178**, 775, 1816 (1924); **179**, 975 (1924); **180**, 637, 833, 1405 (1925). For elementary analysis with potassium dichromate, see also H. Cordebard, *Ann. chim. anal. et chim. appl.*, (2) **3**, 49 (1921); cf *Z anal. Chem.*, **76**, 295 (1929).

[100] H. C. S. Snethlage, *Z. anal. Chem.*, **102**, 321 (1935); *Rec. trav. chim.*, **53**, 567 (1934); cf. B. E. Christensen, R. J. Williams, and A. E. King, *J. Am. Chem. Soc.*, **59**, 293 (1937).

[101] N. F. Schulz, *Anal. Chem.*, **25**, 1762 (1953); cf. A. I. Medalia, *ibid.*, **23**, 1318 (1951).

CHAPTER VI

IODOMETRY. REAGENTS AND THEIR STANDARDIZATION

1. Introduction. Iodine is a relatively weak oxidizing agent with an oxidation potential much lower than that of most oxidizing agents used in volumetric analysis:[1]

$$I_2 + 2e = 2I^- \qquad E_0 = +0.5355 \text{ v.}$$

The low oxidation potential of the system makes iodine much more selective than other oxidizing agents. The system is perfectly reversible, and very sharp end-points are possible in titrations. Iodometric titrations are therefore very valuable and widely used in volumetric analysis. The end-point can also be determined with great accuracy by potentiometric or amperometric methods.

Iodometric titrations may be divided into two classes. Substances with oxidation potentials lower than that of the iodine–iodide system are in general oxidized readily by iodine. These substances can be titrated with standard iodine solution. This type of titration may be referred to as a *direct titration method* and has been used for the determination of reducing agents, such as sulfide, sulfite, thiosulfate, arsenite, and tin(II). Substances having oxidation potentials higher than that of the iodine-iodide system, in general, oxidize iodide to iodine. These substances can be determined by titrating the liberated iodine with standard thiosulfate solution. This type of titration may be referred to as an *indirect titration method* and has been used for the determination of oxidizing agents, such as chlorine, bromine, iodate, dichromate, cerium(IV), iron(III), and copper(II).

Oxidation potentials are influenced by several experimental conditions. One of these is the hydrogen-ion concentration. Since in acid medium hydrogen ions are not involved in the iodine-iodide system, the oxidation potential is not appreciably affected by the hydrogen-ion concentration (in alkaline solutions this is not true because of the hydrolysis of iodine to hypoiodite and the subsequent oxidation to iodate). On the other hand, many of the systems which react with the iodine–iodide system contain oxygen and consequently involve hydrogen ions in their oxidation-reduction reactions. The oxidation potentials of these systems are affected by the pH of the solution, increasing markedly with increasing acidity. An interesting example is the arsenic acid–arsenious acid system.[1] The effect

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[1] W. M. Latimer, *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, 2nd ed., Prentice-Hall, New York, 1952.

$$H_3AsO_4 + 2H^+ + 2e = HAsO_2 + 2H_2O \qquad E_0 = +0.559 \text{ v.}$$

of pH on the potential of this system is given by the equation:[2]

$$E = +0.559 + \frac{0.0591}{2} \log \frac{[H_3AsO_4][H^+]^2}{[HAsO_2]}$$

$$= +0.559 + \frac{0.0591}{2} \log \frac{[H_3AsO_4]}{[HAsO_2]} - 0.0591 \text{ pH}$$

In strongly acid solution, the potential of this system is greater than that of the iodine–iodide system, so arsenic acid oxidizes iodide quantitatively:

$$H_3AsO_4 + 2I^- + 2H^+ \rightleftharpoons HAsO_2 + I_2 + 2H_2O$$

On the other hand, the potential of the arsenic system is lower than that of the iodine system in neutral or faintly acid solutions, so that iodine quantitatively oxidizes arsenious acid.

Acidity also influences the oxidation potential of oxygen markedly. Thus acid solutions of iodide are easily oxidized by air, whereas neutral solutions are relatively stable in air.

Since the oxidation potential of a system depends upon the ratio of the activities (concentrations) of the oxidized and reduced forms, it may be influenced by the addition of a reagent which forms a complex, a slightly dissociated, or a slightly soluble compound with one of the two forms (or with both, if the stabilities or solubilities of the compounds thus formed are different). Ferric iron oxidizes iodide quantitatively:

$$2Fe^{3+} + 2I^- \rightleftharpoons 2Fe^{2+} + I_2$$

and the reaction can be utilized for the iodometric determination of iron. However, if fluoride is added, the ferric iron forms a very stable complex which no longer oxidizes iodide. This phenomenon is used to prevent the interference of iron in the iodometric determinations of other substances.[3] The reaction can be made to go from right to left in the presence of a complex formed when the ferric complex is much more stable than the ferrous complex. This, for example, is true in the presence of ethylenediaminetetraacetate or pyrophosphate. The ferrous iron can be titrated with iodine, but oxygen must be excluded.

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[2] Cf. Vol. I, pp. 74 ff.

[3] Cf. B. Park, *Ind. Eng. Chem., Anal. Ed.*, **3**, 77 (1931).

Cupric copper reacts quantitatively with iodide:

$$2Cu^{2+} + 4I^- = Cu_2I_2 + I_2$$

The oxidation potential of the cupric–cuprous system is more negative than that of the iodine–iodide system but, because of the low solubility of cuprous iodide, the potential of the cupric–cuprous iodide system is more positive than that of the iodine–iodide system and the reaction goes from left to right. If, on the other hand, the cupric copper is masked, e.g., as a citrate, tartrate, or oxalate complex, the reaction can be made to go quantitatively from right to left.[4]

The oxidation potential of the iodine–iodide system can be altered by varying the iodide and (or) iodine concentration. The potential decreases with increasing iodide and decreasing iodine content. The iodine content can be decreased by extraction with organic solvents (e.g., chloroform or carbon tetrachloride), by distillation, or by titration with thiosulfate. Direct iodometric titrations may be assisted by increasing the oxidation potential of iodine. This can be effected by reducing the iodide-ion concentration in the solution, e.g., by adding mercuric salts.[5] By the addition of mercuric chloride to solutions containing arsenic(III) or antimony(III), it is possible to oxidize quantitatively these substances with iodine even in strongly acid solutions. When other oxidizing agents are present which react with iodide but not with bromide or chloride, the distillation should be done from hydrobromic or hydrochloric acid medium. The halogen which distils over is received in an iodide solution and the iodine liberated is then titrated with standard thiosulfate. This modification is useful in the determination of higher oxides such as manganese dioxide in pyrolusite. If iodide were added directly to the sample, iodine would be liberated by the manganese dioxide and also by ferric iron, which is a common impurity. On the other hand, only manganese dioxide liberates chlorine from hydrochloric acid:

$$MnO_2 + 4H^+ + 4Cl^- \longrightarrow Mn^{2+} + Cl_2 + 2Cl^- + 2H_2O$$

$$Cl_2 + 2I^- \Longrightarrow 2Cl^- + I_2$$

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[4] Cf. D. N. Hume and I. M. Kolthoff, *Ind. Eng. Chem., Anal. Ed.*, 16, 103 (1944).

[5] N. H. Furman and C. O. Miller, *J. Am. Chem. Soc.*, 59, 152 (1937).

Iodine is only slightly soluble in water but is readily soluble in solutions of iodide[5a] with the formation of the triiodide ion, I_3^-. The

$$I_2 + I^- = I_3^- \qquad K = 7.68 \times 10^2$$

oxidation potential of the iodine–iodide system is not affected markedly by the formation of triiodide.[1]

$$I_3^- + 2e \rightleftharpoons 3I^- \qquad E_0 = +0.536 \text{ v.}$$

Although the iodine–iodide system is reversible, many iodometric reactions do not proceed rapidly. In addition, many reactions do not proceed directly according to the final stoichiometric equation but often proceed through intermediate steps. From an analytical point of view it is always interesting to know the reaction mechanism in detail because this may lead to better methods of titration for these substances.

As an illustration let us consider the reaction between iodide and anions of oxyhalogen acids:

$$BrO_3^- + 6H^+ + 6I^- \longrightarrow Br^- + 3I_2 + 3H_2O$$

The reaction does not proceed instantaneously or strictly according to the equation as written. According to Bray,[6] hypoiodous acid is formed as an intermediate which reacts rapidly with iodide:

$$\begin{array}{ll} HBrO_3 + HI \longrightarrow HOI + HBrO_2 & \text{(slow)} \\ HOI + HI \longrightarrow H_2O + I_2 & \text{(rapid)} \end{array}$$

The concentration of hypoiodous acid plays a significant role when substances which are oxidized to higher oxygenated compounds are titrated with iodine. Thus, according to Roebuck,[7] the speed of the reaction between iodine and arsenious acid depends on the concentration of hypoiodous acid formed by hydrolysis of iodine and increases with increasing pH of the solution.

If oxygen is not involved in the iodometric reaction, the titration may be very slow under certain circumstances, for it proceeds by way of an intermediate addition product. In this way the slow reactions between iodide and ferric ions[8] and between iodine and titanous ion[9] may be explained.

[5a] M. Davies and E. Goynne, *J. Am. Chem. Soc.*, **74**, 2748 (1952); G. Jones and B. B. Kaplan, *ibid.*, **50**, 1845 (1928).

[6] W. C. Bray, *Z. physik. Chem.*, **54**, 463 (1906).

[7] J. R. Roebuck, *J. Phys. Chem.*, **6**, 365 (1902).

[8] J. N. Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

[9] D. M. Yost and S. Zabaro, *J. Am. Chem. Soc.*, **48**, 1181 (1926).

2. Sources of Error in Iodometry. Two important sources of error in iodometry are the loss of iodine by volatilization and the liberation of iodine by air oxidation of iodide ion.

Iodine is easily volatilized from its solutions. In the presence of an excess of iodide the volatility is decreased markedly through the formation of triiodide ion. At room temperature the loss of iodine by volatilization from a solution containing at least 4 per cent of potassium iodide is negligible provided that the titration is not prolonged unduly. If a solution containing iodine is allowed to stand it should be kept in a glass-stoppered vessel. Titrations should be performed in Erlenmeyer flasks and not in open beakers.

Iodide ion is oxidized by the oxygen in air according to the overall reaction:

$$4I^- + O_2 + 4H^+ = 2I_2 + 2H_2O$$

The rate of reaction is increased by increased acidity and by sunlight. For this reason iodometric titrations should not be performed in direct sunlight, and solutions containing iodide should be kept in amber glass bottles. Many substances catalyze the air oxidation of iodide. Cuprous ion has an appreciable effect; it is readily oxidized by air to cupric, which in turn oxidizes iodide. The slight solubility of cuprous iodide fortunately decreases the rate of air oxidation of copper(I); nevertheless, copper(I) does catalyze the air oxidation of iodide. It has been observed that ferrous, manganous, and chromic ions have almost no effect in acid solutions. *Nitrite ion and nitric oxide cause very marked interference even when present in trace amounts.* Nitrite is reduced to nitric oxide by iodide:

$$2NO_2^- + 2I^- + 4H^+ = 2NO + I_2 + 2H_2O$$

Nitric oxide is quickly air-oxidized to higher oxides of nitrogen which in turn react anew with iodide to form nitric oxide to perpetuate the oxidation of iodide. Iodometric titrations cannot be performed in the presence of oxides of nitrogen; these oxides are usually eliminated by evaporating the solution or by reducing the oxides with organic reagents such as urea[10] and sulfamic acid.[11]

Air-oxidation of iodide may be induced by the reaction between iodide and an oxidizing agent. The induced reaction becomes noticeable especially when the main reaction goes slowly. If an acidified solution of vanadate or ferric is treated with excess iodide, allowed to stand, and titrated with thiosulfate, too much iodine is usually formed. For these determinations, the solution must be freed from air before the addition of iodide. The air may be removed by adding several 200–400 mg. portions of sodium bicarbonate to the acid solution, by passing in a stream of carbon dioxide or by adding dry ice. Potassium iodide is then added and the flask is stoppered immediately. It is best to use glass-stoppered flasks or bottles for these titrations. Whenever an acid solution of iodide has to be allowed to stand for an appreciable period of time, this precaution of removing air from the solution must be taken.

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[10] L. O. Hill, *Ind. Eng. Chem., Anal. Ed.*, 8, 200 (1936).

[11] R. C. Brasted, *Anal. Chem.*, 24, 1040 (1952).

Another possible error may arise from allowing insufficient time for complete reaction. For example, in the indirect iodometric titration of an oxidizing agent sufficient time must be allowed for the reaction with iodide to go to completion before titration with thiosulfate.

For the sake of completeness, we mention the adsorption of iodine on the surface of some precipitates, e.g., those obtained in the bromometric determination of phenol, cresol, and aniline. The liquid and precipitate must be shaken vigorously at the end-point or some alcohol must be added to displace the iodine from the surface.

When iodine is titrated with thiosulfate, the familiar reaction:

$$I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$$

takes place. If the titrated solution is to be used for further determinations, it may be necessary to consider the instability of tetrathionate in the solution. The mechanism of the decomposition of tetrathionate is very complex[12] and is of interest in so far as some of the decomposition products may react again with iodine, e.g., sulfite and thiosulfate. The decomposition is furthered by heat and alkalinity. According to Riesenfeld,[12] the reaction is:

$$2S_4O_6^{2-} + 6OH^- = 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O$$

The decomposition is perceptible also in neutral solutions. Kolthoff has boiled a solution containing 10 ml. of 0.1N iodine, 10 ml. of 0.1N

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[12] Cf. E. H. Riesenfeld and G. W. Feld, *Z. anorg. u. allgem. Chem.*, **119**, 225 (1921); E. Abel, *Monatsh.*, **28**, 1239 (1907); E. V. Espenhahn, *J. Soc. Chem. Ind.*, **36**, 483 (1917); F. Foerster and A. Hornig, *Z. anorg. u. allgem. Chem.*, **125**, 86 (1923); A. Kurtenacker and H. Kaufmann, *ibid.*, **148**, 43, 225, 256, 369 (1925); A. Kurtenacker, *Abegg's Handbuch der anorganischen Chemie*, Vol. IV, Pt. 1, Verlag von S. Hirzel, Leipzig, 1927, p. 541.

thiosulfate, and 5 ml. of 2*N* sodium acetate for one-half hour. The liquid became somewhat turbid with free sulfur, reacted acid, and used up 3 ml. of 0.1*N* iodine or 3 ml. of 0.1*N* alkali (phenolphthalein end-point). In the absence of sodium acetate, and especially in acidic solution, the decomposition is slower. The decomposition is slower at room temperature. A solution containing 10 ml. of 0.1*N* iodine, 10 ml. of 0.1*N* thiosulfate, and 1 g. of sodium bicarbonate was allowed to stand for 24 hours at room temperature. On acidification with acetic acid and titration, 0.4 ml. of 0.1*N* iodine was used.

3. **Determination of the End-Point.** Iodine in aqueous iodide solution has an intense yellow to amber-brown color which can be detected even at very high dilutions. The sensitivity of the color detection is about $5 \times 10^{-5}N$ iodine when viewed through a depth of 8 cm.; this amounts to about 7.5 mg. of iodine per liter or 1 drop of 0.1*N* iodine solution in 100 ml. of water. The end-point in titrations of 0.02*N* and stronger solutions may be detected without the use of an indicator if the solution is colorless.[12a] In order to make the end-point more clearly detectable and to observe the end-point in extremely dilute or in colored solutions, the more pronounced color of the starch-iodine complex is utilized.

Much has been published regarding the nature of the starch-iodine complex. Mylius[13] originally claimed that starch iodide was a chemical compound having the composition $(C_{24}H_{40}O_{20}I)_4HI$. Subsequent observations indicate that the blue color is not due to a true compound having a definite composition but is more likely caused by adsorption of iodine molecules or triiodide ions on or within the colloidal macromolecules of starch.[14]

The intensity and the shade of the starch-iodine color obtained depend on several factors. Systematic investigations of some of the factors which affect the sensitivity of the color reaction have been reported.[15] If the iodide-ion concentration in the solution is greater than $4 \times 10^{-5}M$, the blue color is visible when the iodine concentration is $2 \times 10^{-5}M$ or greater. With greater iodide-ion concentrations, the sensitivity is increased slightly but with lower iodide-ion concentrations the sensitivity is decreased sharply. With pure iodine in the absence of iodide, starch produces no blue color even when sufficient iodine is present to yield a yellow color. The addition of iodide and, to a lesser degree, the addition of other salts, such as alkali and alkaline earth metal halides and sulfates, develop the blue starch-iodide color. Acids like sulfuric and hydrochloric increase the sensitivity to about $1 \times 10^{-5}N$ iodine concentration at 15°C. Mercuric chloride and other substances which complex iodide ions strongly must not be present in excess since they remove iodide ions from the starch and reduce the sensitivity of the starch-iodine color.

[12a] Cf. V. J. Anhorn and H. Hunt, *Ind. Eng. Chem., Anal. Ed.*, **9**, 591 (1937).

[13] F. Mylius, *Ber.*, **20**, 688 (1887); **28**, 385 (1896).

[14] Cf. C. S. Hanes, *New Phytologist*, **36**, 101, 189 (1937); K. Freudenberg, E. Schaaf, G. Dumpert, and T. Ploetz, *Naturwiss.*, **27**, 841 (1939); K. Freudenberg and H. Boppel, *Ber.*, **71B**, 2505 (1938); **73B**, 609 (1940); K. H. Meyer and P. Bernfeld, *Helv. Chim. Acta*, **24**, 389 (1941); K. H. Meyer, in *Advances in Colloid Science*, Vol. I, E. O. Kraemer, ed., Interscience, New York-London, 1942, pp. 177 ff.; R. E. Rundle and R. R. Baldwin, *J. Am. Chem. Soc.*, **65**, 554 (1943); R. E. Rundle and D. French, *ibid.*, **65**, 558, 1707 (1943); R. S. Stein and R. E. Rundle, *J. Chem. Phys.*, **16**, 195 (1948); G. A. Gilbert and J. V. R. Marriott, *Trans. Faraday Soc.*, **44**, 84 (1948).

The sensitivity of the starch-iodine reaction is so high that the indicator blank is negligibly small in titrations with solutions stronger than $0.01N$. With more dilute solutions the indicator blank must be determined under approximately the conditions of the actual titration. Typical titration blanks in the titration of iodine with thiosulfate at room temperature are given in Table I. In the titration of iodine with thiosulfate, the blue color disappears a little too soon, and in titrations with iodine the blue color appears a little late.

TABLE I

Titration Blank in the Titration of Iodine with Thiosulfate at 15°–20°C. (According to Kolthoff)

Nature of solution	Correction (in ml. of $0.001N$ soln.) for final volume of 100 ml.
Neutral or feebly acid	1.5
0.8–$1N$ in sulfuric acid	1.0
0.8–$1N$ in hydrochloric acid	0.6

With higher temperatures the sensitivity of the starch-iodine reaction is decreased. Starch cannot be used as indicator at higher temperatures because of decreased sensitivity and oxidation by iodine (Table II).

Organic substances decrease the sensitivity of the starch-iodine reaction. Some illustrations are given in Table III. The sensitivity of the yellow color

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[15] C. Meineke, *Chem. Ztg.*, **18**, 157 (1894); C. Lonnes, *Z. anal. Chem.*, **33**, 409 (1894); J. Pinnow, *Z. anal. Chem.*, **41**, 485 (1902); E. W. Washburn, *J. Am. Chem. Soc.*, 30, 31 (1908); I. M. Kolthoff, *Pharm. Weekblad,* **56**, 393 (1919); M. S. Nichols, *Ind. Eng. Chem., Anal. Ed.*, **1**, 215 (1929); J. F. Sadusk and E. G. Ball, *ibid.*, **5**, 386 (1933).

TABLE II

Sensitivity of the Starch-Iodine Reaction at Various Temperatures for 0.001N Iodine in 0.002N KI (According to Kolthoff)

Temperature	Sensitivity toward iodine	
15°	$2 \times 10^{-5}N$	
20°	$2.4 \times 10^{-5}N$	
40°	$10 \times 10^{-5}N$	
55°	$22 \times 10^{-5}N$	
65°	$76 \times 10^{-5}N$	(green color)
76°	$160 \times 10^{-5}N$	(dirty green color)
81°	$200 \times 10^{-5}N$	(dirty green color)
87°	$260 \times 10^{-5}N$	(dirty green color)

of iodine is also tabulated. The observations were made with 0.001N iodine in 0.002N potassium iodide. In the presence of much alcohol, the yellow color of iodine is more sensitive than the starch-iodine color and should be used for detecting the end-point.

TABLE III

Effect of Organic Substances on the Sensitivity of the Starch-Iodine Reaction

Solvent	Sensitivity toward iodine	
	Starch-Iodine	Iodine color
Water	$2 \times 10^{-5}N$	$4.5 \times 10^{-5}N$
20% methanol	$12 \times 10^{-5}N$	$4.5 \times 10^{-5}N$
20% ethanol	$10.5 \times 10^{-5}N$	$4.5 \times 10^{-5}N$
40% ethanol	$36 \times 10^{-5}N$	$4.5 \times 10^{-5}N$
50% ethanol	No blue color	$4.5 \times 10^{-5}N$
20% glycerol	$19 \times 10^{-5}N$	$10 \times 10^{-5}N$
8% saccharose	$20 \times 10^{-5}N$	$12 \times 10^{-5}N$
Very dilute pepsin solution	$11 \times 10^{-5}N$	$4.5 \times 10^{-5}N$
The same, with sulfuric acid	$4 \times 10^{-5}N$	$4.5 \times 10^{-5}N$
0.5% gelatin	$32 \times 10^{-5}N$	$22 \times 10^{-5}N$

The shade of the starch-iodine color depends primarily upon the structure and composition of the starch. The unbranched amylose[16] fraction of starch yields a pure blue color; the branched amylopectin fraction yields a purple-to-red color; the more highly branched erythroamylose and erythrogranulose give a red color; the still more highly branched glycogen gives a reddish brown color; and the extremely irregular residual dextrin from glycogen yields a yellow-to-brown color only slightly more intense than the color of iodine alone.[17] The affinity of starches for iodine varies directly with the length of the starch chain and inversely with the degree of branching.

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[16] International Union of Pure and Applied Chemistry, *J. Polymer Sci.*, **8**, 269 (1952); A. M. Patterson, *Chem. Eng. News*, **30**, 3204 (1952).

Preparation of Starch Solution. Many procedures have been suggested for the preparation of a starch solution suitable for iodometric titrations. We find that the preparation by the method of Mutnianski[18] is altogether satisfactory.

Procedure: Make a smooth paste of 2 g. of soluble starch and 10 mg. of mercuric iodide by rubbing with 30 ml. of water. Add the paste to about 1 liter of boiling water; a clear solution should result. If necessary, boil the solution until it becomes clear. Cool and store in a stoppered bottle. Use about 5 ml. of this 0.2 per cent starch solution per 100 ml. of solution to be titrated.

Notes: (1) The mercuric iodide acts as a preservative, and the starch solution should remain clear for long periods even in a clear glass bottle.

(2) If the starch solution fails to give a blue color with iodine and yields instead a violet-to-red color, it should be discarded and a new solution prepared.

Starch has some shortcomings as an indicator in iodometric titrations; chief among these are its insolubility in cold water, the instability of its aqueous dispersions, and the insolubility of its complex with iodine which requires the starch to be added to the solution just before the end-point is reached in indirect titrations. Several modifications of starch have thus been recommended in the literature.

Conner and Bovik[19] suggested the use of a dry preparation of a ground starch which can be sprinkled into the titrated solution. The dry starch is prepared by a procedure similar to that suggested by Alsberg, Griffing, and Field[20] and by Schoch.[21]

Procedure: Suspend a convenient quantity of starch in about twice its weight of ethanol and grind in an efficient ball mill for at least 80 hours. Practically all the starch granules should be disintegrated (observe microscopically). Filter off the ground starch, dry, and then regrind. The resulting preparation is almost completely soluble in cold water and is ready for use.

Notes: (1) Presumably any starch may be prepared by this procedure, but soluble starch is particularly satisfactory.

(2) The dry starch preparation may be conveniently stored and dispensed in a salt or pepper shaker. If preferred, a solution may be prepared with cold water.

[17] K. H. Meyer in *Advances in Colloid Science,* Vol. I, E. O. Kraemer, ed., Interscience, New York-London, 1942, p. 179.

[18] M. Mutnianski, *Z. anal. Chem.*, 36, 220 (1897); cf. also G. Gastine, *Bull. soc. chim. France*, (2) 50, 172 (1888); *Z. anal. Chem.*, 28, 339 (1889).

[19] H. A. Conner and R. W. Bovik, *Ind. Eng. Chem., Anal. Ed.*, 16, 772 (1944).

[20] C. L. Alsberg, E. P. Griffing, and J. Field, *J. Am. Chem. Soc.*, 48, 1299 (1926).

[21] T. J. Schoch, *Cereal Chem.*, 18, 121 (1941).

Starch treated with alkali, then neutralized with acid, was prepared by Platner[22] and observed to show no deterioration, mold growth, loss of reactivity, or production of reddish color with iodine even after 12 months.

Procedure: Suspend about 2 g. of powdered starch in 300–400 ml. of water and add a 20 per cent solution of sodium or potassium hydroxide until a thick, syrupy, almost clear solution is obtained. (About 30 ml. of 20 per cent potassium hydroxide solution is required for 2 g. of potato starch.) Allow the solution to stand for about 1 hour to ensure complete reaction. Neutralize the solution with concentrated hydrochloric acid to the litmus end-point. If acid does not interfere in the iodometric titration in which the starch is used, add 1.0 ml. of glacial acetic acid as preservative.

Note: More recently, several other methods for the preparation of stable starch solutions have been advocated. Nordling[22a] mixes 50 ml. of glycerol and 50 ml. of water and adds a slurry of 1 g. of soluble starch in 2–3 ml. of water to the boiling mixture. This is stirred, boiled for a further 3 minutes and cooled.

Holler[22b] recommends formamide as solvent. A slurry of 5 g. of soluble starch and 30 ml. of formamide is prepared and poured while stirring into 65 ml. of formamide heated to 100–110°C. under a hood. The starch dissolves within 1 minute and the solution is then cooled.

In studies concerning the solvent properties of urea, Clark[22c] noted that starch readily dissolved in molten urea. He prepared a solid solution by refluxing starch and urea (1:19) with xylene (b.p. 132°C.), at which temperature urea melts but decomposition is negligible. When cool, the solid mass was finely powdered. When added to solutions containing iodine, the urea dissolved leaving a very fine suspension of starch which behaved in the same way as normal starch indicator. Clark suggests that this solid solution might be used as a stable starch indicator preparation.

It is probable that certain commercial iodometric indicators sold under various trade-names consist of a solid solution of starch in urea. One such preparation when analyzed [Authors] was found to contain urea and starch in the above proportions.

Since iodine forms the most intensely colored complex with the linear amylose fraction of starch, Liggett and Diehl[23] recommend the use of this fraction instead of whole starch. Amylose may be separated from starch by the method of Schoch[24] or may be obtained commercially from G. Frederick Smith Chemical Co., Columbus, Ohio, as a moist paste under butanol. The moist amylose is readily dispersed in water, but if allowed to dry cannot be dispersed. Butanol does not interfere with the indicator properties; on the contrary, it is helpful since it acts as a preservative. Two to three drops of 1 per cent amylose solution is equivalent to 1 ml. of 1 per cent starch solution as indicator for iodometric titrations. On prolonged standing, aqueous solutions of amylose may become turbid, but this apparently does not impair its color reaction with iodine. Liggett and Diehl observed that with 1 ml. of 1 per cent amylose in 200 ml. of water containing 20 mg. of potassium iodide, an indicator blank amounting to 0.3 ml. of $10^{-3}N$ iodine solution is found. With soluble starch as indicator, the blank amounted to 0.8 ml. of $10^{-3}N$ iodine solution.

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[22] W. S. Platner, *Ind. Eng. Chem., Anal. Ed.*, **16**, 369 (1944).

[22a] W. D. Nordling, *Chemist Analyst*, **42**, 70 (1953).

[22b] A. C. Holler, *Anal. Chem.*, **27**, 866 (1955).

[22c] R. E. D. Clark, *Nature*, **168**, 876 (1951).

[23] L. M. Liggett and H. Diehl, *Anachem News*, **6**, No. 1, 9 (1946); cf. J. L. Lambert, *Anal. Chem.*, **25**, 984 (1953).

[24] T. J. Schoch, *J. Am. Chem. Soc.*, **64**, 2957 (1942).

A derivative of starch was recommended as an indicator in preference to starch for iodometric titrations by Peat, Bourne, and Thrower.[25] The sodium salt of a starch glycolic acid in which the ratio of glycolic acid units to glucose units is approximately 1:10 possesses almost the same color-forming properties as starch but is readily soluble in cold water, stable for months in aqueous solution and forms a water-soluble complex with iodine. Knowles and Lowden[26] observed that sodium starch glycolate is not quite so sensitive as starch.

Preparation of Sodium Starch Glycolate: Disperse 10 g. of starch in 160 ml. of water. Add 30 ml. of 50 per cent sodium hydroxide solution. To the mixture add slowly 5 g. of sodium monochloracetate dissolved in 20 ml. of water at 50 °C. Neutralize the solution with acetic acid and dialyze for 3 days in a cellophane bag, using running water. Precipitate the sodium starch glycolate by adding an excess of alcohol and purify by extracting in a Soxhlet apparatus with 10:90 (by volume) water-alcohol. The glycolic acid content can be estimated by precipitation of either the copper or the silver salt.

Other Indicators: Many organic compounds give the characteristic blue color with iodine. Barger and his coworkers[27] observed that certain colloidally dispersed substances give a blue color with iodine similar to starch. They studied such substances as lanthanum and praseodymium acetate, coumarin and acetocoumarin, and derivatives of α-pyrone, γ-pyrone, xanthone, flavone and thioflavone, and observed that the blue color arises only when the substances are colloidally dispersed. Bergmann[28] studied 1,2-cycloacetals.

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[25] S. Peat, E. J. Bourne, and R. D. Thrower, *Nature*, **159**, 810 (1947); cf. also F. Höppler, *Chem. Ztg.*, **67**, No. 7–8, 72 (1943); W. Theilacker, *Z. anal. Chem.*, **132**, 356 (1951); L. Deibner, *Chim. anal.*, **33**, 207 (1951).

[26] G. Knowles and G. F. Lowden, *Analyst*, **78**, 159 (1953).

[27] G. Barger and E. Field, *J. Chem. Soc.*, **101**, 1394 (1912); G. Barger and W. W. Starling, *ibid.*, **107**, 411 (1915); G. Barger and F. J. Eaton, *ibid.*, **125**, 2407 (1924).

One of the most sensitive of these substances is α-naphthoflavone. Hahn and his coworkers[29] utilized this reagent, and Reith[30] investigated systematically its use as an iodometric indicator. Reith found that true solutions of α-naphthoflavone do not form a colored complex with iodine, colloidal sols instantly form a blue color, and the solid crystalline indicator is colored only weakly by iodine. It is necessary, therefore, that the flavone be present as a sol if it is to be used as an indicator. A 1 per cent solution is prepared in alcohol and 0.5 ml. of this solution added dropwise to 100 ml. of solution. As little as 5 μg. of free iodine can be detected in 100 ml. of solution containing 0.1–0.01 per cent potassium iodide. In the absence of iodide the limit of sensitivity is 30 μg. of iodine per 100 ml. The color obtained depends on the iodine and iodide concentration in the solution. In the titration of iodine with thiosulfate in the presence of iodide the color change is from blue to violet; only when the iodide concentration at the end-point is very low is the change from blue to colorless. With higher concentrations of flavone, it is flocculated and the color intensity of the iodine complex decreases. To circumvent this, the indicator may be added just before the end point.

Reith determined empirical corrections which should be applied to iodometric titrations using this indicator. To 100 ml. of $0.1N$ sulfuric acid, 1 ml. of $10^{-3}N$ iodate and 10 mg. of potassium iodide, he added each the materials listed in Table IV; then, after shaking, he added 0.5 ml. of 0.1 per cent α-naphthoflavone and titrated the solution with $10^{-3}N$ thiosulfate. The corrections given in the table are added to the volume of thiosulfate used.

TABLE IV

Additions	Correction (in ml. of $10^{-3}N$ thiosulfate)	Additions	Corrections (in ml. of $10^{-3}N$ thiosulfate)
—	0.64	1 g. $SO_4^{2-}(K_2SO_4)$	0.66
1 ml. N H_2SO_4	0.55	1 g. $NO_3^-(KNO_3)$	0.69
20 ml. N H_2SO_4	0.70	Temperature	
100 mg. KI	0.65	0°	0.76
1 g. KI	0.86	13°	0.72
1 g. Cl^- (NaCl)	0.62	30°	0.48
1 g. Br^- (KBr)	0.65	43°	0.20

α-Naphthoflavone behaves differently from starch. The sensitivity of the starch-iodine reaction increases with increasing iodide content of the solution, whereas that of the flavone reaction decreases. For starch the titration correction increases with rising temperature, whereas for α-naphthoflavone the correction decreases. Above 70°, however, the flavone gives no blue color with iodine and on cooling the color is very weak since most of the flavone is flocculated.

It is not likely that α-naphthoflavone can replace starch as an iodometric indicator, although in special titrations, such as the microtitration of traces of iodine, it may be superior.

[28] M. Bergmann, *Ber.*, 57, 753 (1924).

[29] M. Hahn, F. Schütz, and F. Pavlidés, *Z. Hyg. Infektionskrankh.*, 108, 439 (1928).

[30] J. F. Reith, *Pharm. Weekblad*, 65, 1097 (1929).

Polyvinyl alcohol also gives a coloration with iodine.[31] Miller and Bracken[32] found that only completely deacetylated polyvinyl alcohol gives a blue color. Polyvinyl alcohol containing 10 mole per cent or more residual acetate groups gives a crimson color which is most sensitive at 20 mole per cent residual acetate. A 1 per cent aqueous solution of polyvinyl alcohol containing 20 mole per cent residual acetate can be used as an iodometric indicator. The preparation is more stable and more sensitive than starch and readily soluble in cold water. At very high dilutions of iodine, the color is brownish yellow and can be seen at an iodine concentration of $3 \times 10^{-6}N$ in a solution containing 2 mg. of potassium iodide per liter and at an iodine concentration of $10^{-5}N$ in a solution containing 0.4 mg. of potassium iodide per liter.

Recently, variamine blue (4-amino-4′-methoxydiphenylamine) has been recommended as an iodometric indicator.[32a] It is necessary to add sodium acetate to raise the pH above 2; otherwise the end-point appears too soon. The pH must also be maintained below 7; at or above this level, no end-point is obtained. The sharpness of the end-point is said to be as good as that of starch and, in some cases, e.g., titration of vitamin C, even better. Most of the conventional titrations may be done with this indicator; the end-point is from blue to colorless on titration with thiosulfate.

Preparation of the Indicator Solution: Grind 1 g. of the hydrochloride with a little water in a mortar, dilute to 100 ml. with water, and filter. The indicator solution has a slight blue-green color. If preferred, the solid indicator mixed with one hundred times its weight of sodium chloride or anhydrous sodium sulfate may be used. Take 100 mg. of this mixture for each titration.

Note: On long standing, the indicator solution decomposes: the solid mixture is more stable. As with starch, the indicator is added when the end-point is approached after first adding sufficient sodium acetate to maintain the pH of the solution above 2.

Triphenylmethylarsonium iodide (0.5 ml. of a 1 per cent aqueous solution and 5 ml. of chloroform or carbon tetrachloride) has been proposed for titration with standard iodine by Gibson and White.[32b] The color change (colorless to yellow-brown) takes place in the organic layer. The indicator is recommended for titration when colored ions are present; copper, however, interferes. There is no indication if this indicator has any advantage over the organic solvents alone.

Organic Liquids for Detection of the End-Point: Before the starch-iodine reaction was used, organic liquids such as benzene, petroleum ether, chloroform, or carbon tetrachloride, which are immiscible with water, were used to detect the end-point in iodometry.[33] The limit of visibility of the reddish violet color of iodine in these solvents exceeds that of the starch-iodine color. On shaking 50 ml. of $4 \times 10^{-5}N$ iodine solution with 10 ml. of chloroform or carbon tetrachloride, the organic phase becomes distinctly violet in color.

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[31] H. Staudinger, K. Frey, and W. Starck, *Ber.*, 60, 1782 (1927); W. O. Herrmann and W. Haehnel, *ibid.*, 1658.

[32] S. A. Miller and A. Bracken, *J. Chem. Soc.*, 1951, 1933.

[32a] L. Erdey, E. Bodor, and M. Papay, *Acta Chim. Acad. Sci. Hung.*, 5, 235 (1955).

[32b] N. A. Gibson and R. A. White, *Anal. Chim. Acta*, 13, 546 (1955).

[33] Rabourdin, *Compt. rend.*, 31, 784 (1850); H. Ditz and B. M. Margosches, *Chem. Ztg.*, 28, 1191 (1904); B. Schwezow, *Z. anal. Chem.*, 44, 85 (1905).

These organic liquids offer many advantages as contrasted with starch for the detection of the end-point in titrations of very dilute or extremely strongly acid solutions and in titrations in which the reaction between iodine and the titrated substance is relatively slow. On the other hand, there are the disadvantages that the titration must be made in bottles or flasks with ground-glass stoppers, the vessel must be well shaken after each addition of reagent, and some time must be allowed for the separation of the two liquid phases.

4. Reaction between Iodine and Thiosulfate. One of the most important reactions in iodometry is that between iodine and thiosulfate in which thiosulfate is oxidized to tetrathionate by iodine:

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

Stronger oxidizing agents, such as bromine, chlorine, permanganate, dichromate, and cerium(IV), oxidize thiosulfate to sulfate in varying amounts depending on experimental conditions. For this reason, these substances are best determined by adding an excess of iodide before titrating with thiosulfate.

Hypoiodite is a stronger oxidizing agent than iodine and oxidizes thiosulfate to sulfate. Topf[34] observed that iodine even in very weakly acid solution contains sufficient hypoiodite from the hydrolysis of iodine to give a detectable amount of the side reaction:

$$S_2O_3^{2-} + 4I_2 + 10OH^- \longrightarrow 2SO_4^{2-} + 8I^- + 5H_2O$$

It follows from this reaction that, with increasing hydroxyl-ion concentration, increasing amounts of thiosulfate are oxidized to sulfate. This was observed by Topf. Abel[35] found that the reaction even went quantitatively to sulfate in strongly alkaline solution; iodate is not involved in the process. Various investigators have confirmed the results of Topf.

The reaction of iodine with thiosulfate has been investigated extensively.[36] The extent to which the side reaction of thiosulfate to sulfate proceeds depends upon several factors: (1) hydroxyl-ion concentration, (2) concentration of iodine and iodide, (3) temperature, and (4) presence of foreign substances. The effect of the various factors is difficult to investigate separately since hypoiodous acid is unstable and since the error depends somewhat upon the speed of titration.

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[34] G. Topf, *Z. anal. Chem.*, 26, 137 (1887).

[35] E. Abel, *Z. anorg. Chem.*, 74, 395 (1912); cf. also W. C. Bray, M. E. Simpson, and A. A. MacKenzie, *J. Am. Chem. Soc.*, 41, 1376 (1919).

[36] Cf. I. M. Kolthoff, *Pharm. Weekblad*, 56, 572 (1919); *Z. anal. Chem.*, 60, 341 (1921).

As stated above, the titration of iodine with thiosulfate cannot be carried out in alkaline solution. The allowable pH depends on the iodine concentration. In order to obtain quantitative oxidation of thiosulfate to tetrathionate by iodine, the pH should be less than 7.6 for the titration of $0.1N$ iodine solutions; less than 6.5 for $0.01N$ iodine solutions; and less than 5 for $0.001N$ iodine solutions. Very dilute solutions must therefore be distinctly acid for the titration. It is especially important that iodine solutions be made acid before titration with standard thiosulfate solutions containing basic materials, such as borax, as stabilizers. Rands[37] observed that a neutral iodine solution titrated with $0.1N$ thiosulfate solution containing 3.8 g. of borax per liter required about 5 per cent less thiosulfate solution than the same amount of iodine solution titrated with neutral thiosulfate. The addition of sulfuric acid to the iodine solution brings the titrations with the two thiosulfate solutions into agreement. Ordinarily iodine in quite strongly acid solution may be titrated accurately if care is taken to stir the solution well to avoid local excess of thiosulfate which decomposes in acid solution to sulfite which in turn is oxidized to sulfate. In strongly acid solution, care must be exercised to avoid air-oxidation of iodide.

In certain titrations, it is necessary to neutralize an acid solution of iodine before titration with thiosulfate (cf. the determination of iodide, p. 252). The neutralization should not be made with excess carbonate, bicarbonate, phosphate, or borax; otherwise the solution becomes too alkaline and errors result. In Table V are given some examples of the possible errors. If acid iodine solutions must be neutralized before titration, a buffer solution should be used to maintain the pH of the solution at the desired value. If the titration must be carried out in an alkaline medium, a standard solution of arsenious acid should be used instead of thiosulfate. For these titrations, an acid solution may be neutralized with an excess of bicarbonate; however, it is better to use borax or disodium phosphate since there is the possibility of losing iodine with the carbon dioxide evolved if bicarbonate is used.

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[37] R. Rands, *Chemistry & Industry*, 1952, 1001.

TABLE V

Titration of 25 Ml. of 0.1N Iodine with 0.1N Thiosulfate

Substance added to iodine solution	Thiosulfate used (ml.)	Per cent error
0.5 g. of sodium carbonate	24.00	−4.0
2.0 g. of sodium carbonate	22.60	−9.6
25 ml. of 0.2M sodium bicarbonate	24.35	−2.5
25 ml. of 0.2M disodium phosphate	24.40	−2.3
25 ml. of 0.2M borax	23.20	−7.1
2 ml. of 2N ammonium carbonate	18.25	−27.0
5 ml. of 2N ammonium carbonate	15.75	−37.0
10 ml. of 2N ammonium carbonate	15.50	−38.0

Angelescu and Popescu[38] utilized the error in the titration of alkaline iodine solutions with thiosulfate to evaluate the hydrolysis constant for iodine:

$$K = \frac{[H^+][HOI][I^-]}{[I_2]}$$

From titration data for iodine in 0.1–0.5N potassium iodide solutions containing sodium bicarbonate, they obtained values for the hydrolysis constant of 0.74×10^{-10} at 20° and 1.43×10^{-10} at 30°C. From titrations of iodine solutions containing no added iodide, they found a value for K at 20° of 1.5×10^{-13}. The latter value is in fair agreement with the values 3×10^{-13} from the work of Bray and Connolly[39] and 4.6×10^{-13} from the work of Horiguchi and Hagisawa.[40]

In the titration of thiosulfate with iodine, the error due to the side reaction in weakly alkaline medium is much less than that for the titration of iodine with thiosulfate. In the presence of bicarbonate, borax, or secondary phosphate, the reaction between iodine and thiosulfate is sufficiently rapid that the iodine does not react with hydroxyl ion to form hypoiodite.

The error in the determination of traces of iodine depends both on the pH of the solution and on the iodide concentration. In working with approximately 0.0003N iodine solutions (obtained from the reaction of chlorine with iodide), Hallinan and Thompson[41] obtained correct results when the value of the expression, 20 pH − 14 log {KI}, was smaller than 100. In this expression {KI} denotes the number of grams of potassium iodide per liter of solution. Thus, if the pH of the sample is 5.7, the concentration of iodide should be about 10 g. per liter or greater.

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[38] E. Angelescu and V. D. Popescu, *Z. physik. Chem.*, **A156**, 304 (1931).

[39] W. C. Bray and E. L. Connolly, *J. Am. Chem. Soc.*, **33**, 1485 (1911); W. C. Bray, *ibid.*, **32**, 932 (1910).

[40] G. Horiguchi and H. Hagisawa, *Bull. Inst. Phys. Chem. Research* (*Tokyo*), **22**, 661 (1943).

[41] F. J. Hallinan and W. R. Thompson, *J. Am. Chem. Soc.*, **61**, 265 (1939)

In the titration of N or $0.1N$ iodine in neutral potassium iodide solution with N or $0.1N$ thiosulfate, the reaction to tetrathionate proceeds normally. If an alcoholic solution of iodine containing no iodide is used, the oxidation potential of iodine is increased so that

$$E = E_0 + 0.0591 \log \frac{[I_2]}{[I^-]^2}$$

thiosulfate is oxidized partially to sulfate and the solution simultaneously becomes acid. If the alcoholic solution of iodine contains iodide, the reaction to tetrathionate again proceeds normally.

Substances which tie up iodide ion, such as mercuric salts, increase the oxidation potential of the iodine–iodide system,[42] which might lead to the oxidation of thiosulfate to sulfate.

The kinetics of the reaction between iodine and thiosulfate was studied by Griffith and his coworkers,[42a] who studied the stoichiometry of the reaction under various conditions, and by Awtrey and Connick,[42b] who applied a flow method to study the kinetics directly. The reaction rate is expressed by the equations:

$$\frac{d[I_2]}{dt} = k_1 \frac{[S_2O_3I^-]^2[I^-]^2}{I_3^-} - 3k_2[S_2O_3I^-]$$

and

$$\frac{d[S_2O_3I^-]}{dt} = -2k_1 \frac{[S_2O_3I^-]^2[I^-]^2}{[I_3^-]} - k_2[S_2O_3I^-]$$

which are explained by the mechanism:

$$\begin{aligned} S_2O_3I^- &= S_2O_3^{2-} + I^+ \\ S_2O_3^{2-} + S_2O_3I^- &= S_4O_6^{2-} + I^- \\ I^- + I^+ &= I_2 \\ I_2 + I^- &= I_3^- \\ 2S_2O_3I^- &= 2S_2O_3^- + I_2 \\ 2S_2O_3^- &= S_4O_6^{2-} \end{aligned}$$

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[42] N. H. Furman and C. O. Miller, *J. Am. Chem. Soc.*, **59**, 152 (1937).

[42a] R. O. Griffith and R. Irving, *Trans. Faraday Soc.*, **45**, 305 (1949); G. Dodd and R. O. Griffith, *ibid.*, p. 546.

[42b] A. D. Awtrey and R. E. Connick, *J. Am. Chem. Soc.*, **73**, 1341 (1951).

5. Reaction between Iodine and Arsenious Acid. In slightly alkaline solution, arsenic trioxide is oxidized quantitatively to the pentavalent oxidation state by iodine:

$$H_3AsO_3 + I_2 + H_2O \rightleftharpoons HAsO_4^{2-} + 4H^+ + 2I^-$$

The reaction is reversible, and from the equation it is seen that the state of equilibrium is dependent greatly on the hydrogen-ion concentration in the solution. Liebhafsky[43] reviewed the data of Roebuck[44] and obtained a value for the equilibrium constant of the reaction:

$$K \quad \frac{[H_3AsO_4][H^+]^2[I^-]^3}{[I_3^-][H_3AsO_3]} \quad 1.6 \times 10^{-1}$$

To evaluate the effect of pH on the reaction, it is necessary to consider in addition the ionization of arsenic acid:

$$H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^-$$
$$H_2AsO_4^- \rightleftharpoons H^+ + HAsO_4^{2-}$$
$$HAsO_4^{2-} \rightleftharpoons H^+ + AsO_4^{3-}$$

From a consideration of the free energies of these substances, Latimer[45] reports the values of the three ionization constants for arsenic acid as $K_1 = 2.5 \times 10^{-4}$, $K_2 = 5.6 \times 10^{-8}$, and $K_3 = 3 \times 10^{-13}$.

Washburn[46] obtained a value for the equilibrium constant of the reaction between iodine and arsenious acid and from this calculated that the pH must lie between 4 and 9 if a titration of arsenious acid with iodine is to be accurate to 0.1 per cent. Thiel and Meyer[47] tested this conclusion experimentally; they limited the pH at the end-point to between 5.8 and 7.5. If the pH is less than 5.8, quantitative results can be obtained but the speed of the reaction is so small that the end-point is reached very slowly. Kolthoff[48] has found that the reaction is still quantitative at pH 3.5, although the reaction then requires a very long time. On the alkaline side, the arsenious acid solution may be quite strongly alkaline if it contains iodide; thus, if arsenious acid is titrated with iodine, the pH may be between 5 and 11.

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[43] H. A. Liebhafsky, *J. Phys. Chem.*, 35, 1648 (1931).

[44] J. R. Roebuck, *ibid.*, 6, 365 (1902); 9, 727 (1905).

[45] Ref. 1, p. 115; cf. also E. W. Washburn, *J. Am. Chem. Soc.*, **30**, 31 (1908).

[46] E. W. Washburn, *J. Am. Chem. Soc.*, 30, 31 (1908); E. W. Washburn and E. K. Strachan, *ibid.*, 35, 681 (1913).

[47] A. Thiel and E. Meyer, *Z. anal. Chem.*, 55, 177 (1916); *J. Soc. Chem. Ind.*, 35, 631 (1916).

[48] I. M. Kolthoff, *Z. anal. Chem.*, 60, 393 (1921); *Pharm. Weekblad*, 56, 621 (1919); *ibid.*, 1322; *ibid.*, 58, 727 (1921).

For titrations of iodine with arsenious acid, the conditions are slightly different. Up to a pH of 9.2 (at the end of the titration) the reaction proceeds quantitatively, so that, even in the presence of excess sodium bicarbonate or ammonium carbonate, quantitative results are obtained. This is in contrast with the titration of iodine with thiosulfate, in which the presence of ammonium carbonate introduces errors of more than 20 per cent. At pH values higher than 9.2 some iodine reacts with hydroxyl ion and escapes titration by forming iodate. Ammonia acts peculiarly. Although it makes the solution more alkaline than sodium carbonate, its interference is only slight (about 0.7–1 per cent). At the beginning of the titration a dark coloration of nitrogen triiodide appears and changes to the yellow iodine-iodide color as the titration proceeds. As in the reverse titration, acid solutions of iodine react very slowly with arsenious acid, especially if starch is present. In order to titrate conveniently $0.1N$ or $0.01N$ iodine with arsenious acid solution directly to the end-point, the pH at the beginning of the titration must lie between 5.5 and 9.5, and at the end-point must lie between 5.0 and 9.0. In special instances, the pH may be as low as 3.5, but for these determinations half an hour or longer may be required because of the slowness of the reaction.

6. Regeneration of Iodine on Acidification of an Alkaline Iodine-Iodide Solution. King and Jette[49] observed that the amount of iodine liberated from potassium iodide by potassium peroxydisulfate in neutral solution agrees with that liberated by an equivalent amount of potassium permanganate in acid solution. On the other hand, when iodine is liberated in alkaline solution and the solution is acidified just before titration, e.g., by Müller's method,[50] the results obtained are consistently 0.2 to 0.5 per cent low. Kurtenacker and Kubina[51] found that under certain conditions the error is about 10 times as large. These results were thoroughly investigated by Köhne,[52] who found that the error increases with decreasing iodine concentration. Working with $0.1N$ solutions, he obtained small errors which confirm the results of King and Jette. On the other hand, working with $0.01N$ solutions, he obtained larger errors like those found by Kurtenacker and Kubina. Large amounts of neutral salts tend to increase the error.

King and Jette suggest that the error results from the decomposition of hypoiodite which is formed as an intermediate:

[49] C. V. King and E. Jette, *J. Am. Chem. Soc.*, **52**, 608 (1930).

[50] E. Müller, *Z. anal. Chem.*, **52**, 299 (1913).

[51] A. Kurtenacker and H. Kubina, *Z. anal. Chem.*, **83**, 14 (1931).

[52] M. Köhne, *Z. anal. Chem.*, **88**, 161 (1932).

$$2IO^- \longrightarrow 2I^- + O_2$$

However, they did not prove this assumption. It is possible that the error arises from a trace of impurity in the reagents, although Köhne found no significant amounts of impurity when he tested. Another possible source of error is the volatilization of traces of iodine by the heat generated when the solution is neutralized.

Van der Meulen[53] tested Müller's method for determining peroxydisulfate with potassium iodide containing a trace impurity of methanol and obtained very large errors.

Although the decomposition of a pure alkaline iodine solution is not definitely ascertained, it is advisable that a blank titration be run on the reagents under the conditions of the determination when working with alkaline solutions of iodine.

7. Mercuric Iodometry. Mercuric salts, including mercuric chloride, increase the oxidation potential of iodine solutions since iodide reacts with these substances to form slightly dissociated mercuric iodide and mercuric iodide complexes. The oxidation potential is increased to such an extent that an "autoxidation" of iodine to iodate takes place, removing free iodine from the solution. In neutral solution, the reaction, according to Furman and Miller,[54] is:

$$6I_2 + 6H_2O + 6HgCl_2 \longrightarrow 5HgI_2 + Hg(IO_3)_2 + 12HCl$$

In acid solution, the iodate reacts with iodide to reform iodine.

When an excess of a strong oxidizing agent, such as bromate, is added to iodide in the presence of mercuric salt and acid, the iodide is oxidized directly to iodate without intermediate formation of free iodine. This led Smith[55] to report no reaction to take place, which he attributed to a "preventive effect" of the mercuric halide complexes.

Furman and Miller determined the effect of mercuric salts on the oxidation potential of the iodine–iodide system. Some of their results are presented in Table VI. The potential of a platinum electrode in solutions 0.01*N* in iodine and 0.01*N* in potassium iodide was measured against the saturated calomel electrode at 25 °C. at various concentrations of acid, with and without mercuric salts present. Since the potential of the saturated calomel electrode is +0.246 v. with respect to the normal hydrogen electrode, the oxidation potential of the iodine–iodide system against the normal hydrogen electrode is greater than the values in Table VI by 0.246 v.

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[53] J. H. van der Meulen, *Z. anal. Chem.*, 88, 173 (1932).

[54] N. H. Furman and C. O. Miller, *J. Am. Chem. Soc.*, 59, 152 (1937); cf. also K. Brückner, *Monatsh.*, 27, 341 (1906); 28, 961 (1907); V. Hovorka, *Collection Czech. Chem. Communs.*, 2, 559, 608 (1930); 3, 285 (1931).

[55] G. F. Smith, *J. Am. Chem. Soc.*, 45, 1417 (1923).

TABLE VI

	E vs. S.C.E. (volt) at the following acid normalities:				
	0	1	2	4	6
Hydrochloric acid	0.400	0.395	0.376	0.345	0.294
HCl + 2 g. $HgCl_2$/50 ml. soln.	0.760	0.662	0.628	0.586	0.531
Sulfuric acid	0.404	0.404	0.397	0.379	0.351
H_2SO_4 + 2 g. $HgSO_4$/50 ml. soln.	0.939	0.971	0.980	0.994	1.008

Since the oxidation potential of the solution is increased by mercuric chloride, many substances which normally are not oxidized or are oxidized only partially by iodine can be determined by mercuric iodometry. As examples, arsenic(III) and antimony(III) are normally titrated with iodine at fairly high pH since the reaction is reversed in very acidic solutions. When an excess of mercuric chloride is added, however, these substances can be determined even in very acid solutions. Since the iodide concentration is made negligibly small by the excess mercuric salt, starch cannot be used as an indicator for the end-point. Furman and Miller used carbon tetrachloride to observe when excess iodine is present in the solution and obtained good results. For the titration of arsenic(III), their solution contained 50 ml. of saturated mercuric chloride and was 1.2 to 1.7N in hydrochloric acid. To titrate antimony(III), they dissolved potassium antimony tartrate in 20 ml. of water, added 50 ml. of N hydrochloric acid saturated with mercuric chloride, and titrated with iodine solution. Carbon tetrachloride is added and the solution is shaken vigorously during titration. The end-point is obtained when the carbon tetrachloride retains the violet color of iodine. Instead of the iodine solution, a potassium iodate solution may be used for the titration (see p. 456).

8. Solutions for Iodometry. ***Iodine in Potassium Iodide Solution:*** A standard solution of iodine can be prepared readily by weighing out pure iodine and dissolving in a potassium iodide solution.

Purification of Iodine: Pure iodine is prepared conveniently by sublimation, according to Treadwell.[56] Commercial iodine is contaminated with chlorine, bromine water, and sometimes cyanide. For the purification, rub 10–12 g. of iodine with 1 g. of potassium iodide and 2 g. of ignited lime. Place the intimate mixture in a dry 250 ml. beaker, B, Fig. 1, or a dry casserole.[57] The flask, K, containing water at room temperature, is set in place, and the beaker, protected by asbestos or a muffle, is heated gently over a small Bunsen flame. The iodine sublimes quickly and forms a crystalline crust on the lower end of the flask. Almost no iodine is lost. When no more violet vapor is present in the beaker, the sublimation is complete. Lift the flask, K, from the beaker with the iodine adhering. To remove the iodine, pass cold water through the flask from *a* to *b*. The flask contracts on cooling and the iodine crystals can be removed readily. Collect the crystals on a watch glass, break up the crystals into large pieces, and repeat the sublimation without adding potassium iodide. Carry out the resublimation at as low a temperature as possible in order to obtain the iodine free of iodide. (If the commercial preparation was quite pure to begin with, a single sublimation with potassium iodide and lime should be sufficient.) Grind the second sublimate in an agate mortar, place on a watch glass, and dry over calcium chloride in an ungreased desiccator. Sulfuric acid, if used as desiccant instead of calcium chloride, may contaminate the product.

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[56] F. P. Treadwell and W. T. Hall, *Analytical Chemistry*, Vol. II, 9th ed., Wiley, New York, 1942, pp. 587–588.

[57] C. R. McCrosky, *J. Am. Chem. Soc.*, **40**, 1664 (1918).

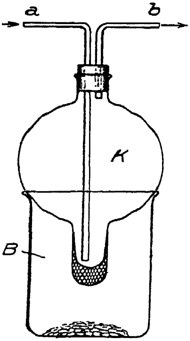

Fig. 1. Apparatus for preparing iodine by sublimation.

Very pure iodine was prepared by Ponndorf.[58] The iodine was precipitated from acidified potassium iodide solution with sodium nitrite, filtered, washed, steam distilled, filtered on a glass filter, sucked as dry as possible, and dried in a vacuum desiccator. The dry product was sublimed in a stream of nitrogen or carbon dioxide and then twice fractionally distilled at 120°C.

Other methods have been proposed for purifying iodine: Stas dissolved the iodine in concentrated potassium iodide solution and precipitated it by adding much water.[59] Musset[60] fused iodine under a concentrated potassium iodide solution to free it of bromine and chlorine. Meineke[61] improved the process to remove cyanogen by using a solution containing calcium chloride, potassium iodide, and hydrochloric acid instead of potassium iodide alone. The iodine obtained was sublimed twice with barium oxide added the first time. Meineke[62] also prepared pure iodine from the reaction of pure potassium hydrogen iodate with potassium iodide and sulfuric acid. The iodine is then sublimed first with, then without, barium oxide. De Koninck[63] heated pure powdered potassium iodide with powdered potassium dichromate and condensed the iodine in a tared flask which is used for weighing. Ladenburg[64] converted pure potassium iodide to silver iodide, removed bromide and chloride by shaking with concentrated ammonia for 24 hours, reduced the silver iodide with zinc and sulfuric acid, precipitated iodine with nitrous acid, distilled with steam, and dried the product over calcium chloride. Lean and Whatmough[65] prepared pure cuprous iodide from copper sulfate, potassium iodide, and sulfur dioxide in water; cuprous bromide and chloride are more soluble. The cuprous iodide can be heated without decomposition in a stream of carbon dioxide to remove hydriodic acid, iodine, and water; then heated to 240°C. in a stream of dry air to liberate iodine, which is condensed readily free of copper salts.

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[58] W. Ponndorf, *Z. anal. Chem.*, 84, 289 (1931).

[59] Cf. A. Gross, *J. Am. Chem. Soc.*, 25, 987 (1903); C. Meineke, *Chem. Ztg.*, 16, 1219 (1892).

[60] F. Musset, *Z. anal. Chem.*, 30, 45 (1891).

Very pure iodine appears blacker and less volatile than ordinary iodine. When pure iodine is stored, it must not be allowed to contact organic substances and must be shielded especially from dust. It is kept best in an ungreased desiccator over calcium chloride.

Preparation of 0.1N Iodine Solution:[66] Into a large glass-stoppered weighing bottle, put approximately 40 g. of potassium iodide (iodate free) and dissolve in 10 ml. of water. Allow the bottle and contents to stand and come to room temperature; then stopper the bottle and weigh accurately. As quickly as possible and without splashing, introduce about 12.7 g. of pure iodine (previously weighed on a rough balance). Restopper the bottle and reweigh accurately. Transfer the solution rapidly and quantitatively into a liter volumetric flask; then fill to the mark with distilled water. Shake until the solution is uniform and transfer to a glass-stoppered, amber glass bottle. Store the solution in a cool, dark place.

The potassium iodide makes the solution more stable by increasing the solubility of iodine and decreasing its volatility through the formation of triiodide ion. In the above preparation, the standard iodine solution is made 4 per cent in potassium iodide as recommended by Chapin.[67] Other workers[68] have found that solutions containing 2 per cent or more of potassium iodide are almost equally stable. The potassium iodide used in the preparation of standard iodine solution must not react alkaline to phenolphthalein in a 10 per cent solution. Moreover, 10 ml. of this solution must not appear yellow when acidified with 1 ml. of 4*N* sulfuric acid, nor give a blue color with starch.

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[61] C. Meineke, *Chem. Ztg.*, 16, 1219 (1892).

[62] C. Meineke, *Chem. Ztg.*, 19, 2 (1895).

[63] L. L. de Koninck, *Brit. assoc. belge des chim.*, 17, 157 (1903); cf. *Chem. Zentr.*, **1903**, **I**, 1435, II, 523.

[64] A. Ladenburg, *Ber.*, **35**, 1256 (1902).

[65] B. Lean and W. H. Whatmough, *J. Chem. Soc.*, 73, 148 (1898).

[66] Cf. K. L. Milstead, *J. Assoc. Offic. Agr. Chemists*, **22**, 567 (1939).

[67] R. M. Chapin, *J. Am. Chem. Soc.*, **41**, 351 (1919).

[68] Cf. E. W. Washburn, *J. Am. Chem. Soc.*, **30**, 31 (1908); F. O. Rice, M Kilpatrick, Jr., and W. Lemkin, *ibid.*, **45**, 1361 (1923); S. Popoff and J. L. Whitman, *ibid.*, **47**, 2259 (1925).

In the conventional method of weighing iodine for standard solutions as given in the procedure above, Popoff and Whitman[69] observed a fairly constant loss of 0.2 mg. every time the stopper is removed from the weighing bottle containing potassium iodide solution. They, therefore, designed a special weighing bottle (Fig. 2). Onto the top of a weighing bottle are sealed two tubes having about 3 mm. internal diameter. One tube has a stopcock and a funnel bulb through which solutions may be introduced, and the other tube is a U-tube vent containing 50 per cent potassium iodide solution. With the stopcock open, weigh the assembly accurately. Add the desired amount of purified iodine, stopper the bottle, close the stopcock, and reweigh the assembly accurately. Now add the desired amount of 50 per cent potassium iodide to the funnel and introduce it slowly into the bottle by opening the stopcock. Air containing iodine vapor is vented through the U-tube, but the iodine is retained by the potassium iodide solution. The bulb on the top of the U-tube helps to keep the solution from being lost, but the rate of bubbling should be controlled to be sure that no solution is lost. When the iodine dissolves, add water through the stopcock almost to fill the bottle. Finally, transfer the solution quantitatively to the desired vessel.

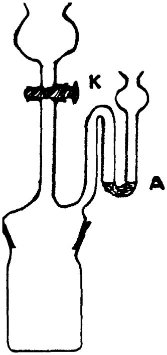

Fig. 2. Apparatus for weighing iodine.

Bawden and Dyche[70] suggested a method of weighing iodine without the use of special apparatus. Iodine (approximately 1 g.) dissolved in 20 ml. of solution which contains 2 parts glycerol and 1 part saturated potassium iodide shows no appreciable loss of iodine and very little loss of water when allowed to stand in an open beaker. The weight of iodine added is obtained by weighing the solution before and after the addition of iodine. The presence of glycerol interferes with

[69] S. Popoff and J. L. Whitman, *J. Am. Chem. Soc.*, 47, 2259 (1925).

[70] A. T. Bawden and S. K. Dyche, *Ind. Eng. Chem., Anal. Ed.*, 5, 347 (1933).

the starch end-point, but the "dead stop" method of Foulk and Bawden[71] may be used to detect the end-point. The end-point can also be found amperometrically. This method of preparation of standard iodine solutions is not recommended. In principle, it is advisable to avoid the addition of foreign substances, especially organic materials, to standard iodine solutions.

Because of the volatility of iodine, the stock solution bottle should be stoppered tightly when not in use and should be opened for as short a time as possible when needed. For the same reason, a burette (a glass stopcock and not pinchcock type should be used) containing iodine solution should not stand open for more than a very short time. Furthermore, iodine solutions should be titrated in Erlenmeyer flasks and not open beakers. If the solution containing excess iodine must be set aside for any period of time, the flask should be glass stoppered (cf. p. 30).

Iodine solution, stored in an ordinary glass container for a long period of time, may contain small amounts of iodate.[72] Glass may give off small amounts of alkali which disproportionate iodine to iodide and iodate. When such a solution is used to titrate arsenite in neutral solution, only the free iodine remaining reacts. On the other hand, if the iodine solution is first acidified, then neutralized and titrated with arsenite, all the iodine is recovered and the titer agrees with that obtained with standard thiosulfate solution. It is best, therefore, to store standard iodine solutions in alkali-resistant glass.

For titrations requiring excess iodine in acid solution the iodine may be prepared *in situ* by allowing a standard potassium iodate solution to react with excess potassium iodide in acid solution.

Sodium Thiosulfate Solution. *Purification of the Salt:* According to Meineke,[73] pure sodium thiosulfate is obtained by recrystallizing reagent grade, commercial preparation several times from water and grinding with alcohol to a fine powder. The paste thus obtained is washed on a suction filter with ether, and air is drawn through to remove the ether. The salt is then removed from the filter and dried in air for 24 hours. Meineke found the resulting product to be 99.99 per cent pure.

A better method of preparation of pure sodium thiosulfate is the following. Recrystallize the salt several times from water, dry in air, grind to a fine powder and complete the drying in a hydrostat over deliquescent calcium chloride hexahydrate. In this way, pure salt having the composition $Na_2S_2O_3 \cdot 5H_2O$ is obtained. The pentahydrate is stable over a wide range of relative humidity at room temperature, viz., between 23.4 and 79.9 per cent at 20° C.[74]

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[71] C. W. Foulk and A. T. Bawden, *J. Am. Chem. Soc.*, **48**, 2045 (1926).

[72] C. K. Banks, *J. Am. Pharm. Assoc.*, **37**, 6 (1948); E. Deiss, *Chem. Ztg.*, **38**, 413 (1914).

[73] C. Meineke, *Chem. Ztg.*, **18**, 33 (1894).

Tests of the Purity of Sodium Thiosulfate. Insoluble Matter (Sulfur): A 10 per cent solution of the salt must be perfectly clear.

Alkaline Material: Twenty-five milliliters of 10 per cent solution should be neutral to methyl yellow and after the addition of 1 drop of 0.1*N* hydrochloric acid should assume the transition color. Sensitivity, 0.02 per cent $Na_2CO_3 \cdot 10H_2O$.

Sulfate-Sulfite: Treat 5 ml. of 10 per cent solution of the salt with a normal solution of iodine in neutral potassium iodide until the liquid is pale yellow. Add several drops of 4*N* acetic acid and some barium chloride or nitrate solution. No turbidity should be detected after 5 minutes standing. Sensitivity, 0.01 per cent $Na_2SO_4 \cdot 10H_2O$ or $Na_2SO_3 \cdot 7H_2O$. The sulfate test cannot be made directly on the thiosulfate solution since the thiosulfate hinders the crystallization of barium sulfate.

Sulfite: A solution in which the thiosulfate is oxidized by excess iodine as in the sulfate-sulfite test should react neutral to methyl yellow after the excess iodine is removed with thiosulfate solution. Sulfite in the thiosulfate produces an acid reaction:

$$SO_3^{2-} + I_2 + H_2O \longrightarrow SO_4^{2-} + 2I^- + 2H^+$$

Sensitivity, 0.01 per cent $Na_2SO_3 \cdot 7H_2O$.

Chloride: Treat 5 ml. of 10 per cent solution with 5 ml. of 4*N* nitric acid free of chloride; heat 10 to 15 minutes on a hot water bath, filter, and treat the solution with silver nitrate. The opalescence obtained should not exceed that of a nitric acid solution containing 3 mg. of chloride per liter after treatment with silver nitrate. Sensitivity, 0.01 per cent NaCl.

Sulfide: A 10 per cent solution must not become dark colored on treatment with lead acetate. Sensitivity, 0.01 per cent $Na_2S \cdot 3H_2O$.

Heavy Metals: Ten milliliters of 10 per cent solution should remain clear and colorless after the addition of 3 drops of *N* sodium sulfide.

Calcium: Five milliliters of 10 per cent solution should show no turbidity on standing 5 minutes after adding 3 drops of 0.5*N* ammonium oxalate solution and several drops of ammonia. Sensitivity, 0.005 per cent Ca.

Stability of Sodium Thiosulfate Solutions: According to LaMer and Tomlinson,[75] solid sodium thiosulfate pentahydrate decomposes to a slight extent upon standing at room temperature for several months to form sulfur and a substance qualitatively identified as sodium sulfite. Recrystallization from water removes these impurities. Solutions prepared from old and from freshly recrystallized salt are equally stable and useful as analytical reagents but behave differently in kinetic studies.

Solutions of sodium thiosulfate slowly change in titer with lapse of time; many reasons have been given for this. The mechanism of the decomposition is very complex; thus, in systematic studies, many irregularities and contradictions are reported.[76]

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[74] *International Critical Tables*, E. W. Washburn, ed., McGraw-Hill, New York, Vol. 3, 1928, p. 372; Vol. 7, 1930, p. 305.

[75] V. K. LaMer and H. M. Tomlinson, *Ind. Eng. Chem., Anal. Ed.*, 9, 588 (1937).

Several factors contribute to the decomposition of thiosulfate solutions:

(*a*) Acidity: Thiosulfate ion in neutral or alkaline solution is relatively stable; however, neither hydrogen thiosulfate salts nor thiosulfuric acid is stable. The decomposition process is complicated, but the known facts seem to be the following.[77] If the hydrogen-ion concentration in the solution is greater than about 2.5×10^{-5} *M*, the very unstable hydrogen thiosulfate ion apparently forms and decomposes:

$$HS_2O_3^- \longrightarrow HSO_3^- + S$$

A second, slower reaction results in the formation of pentathionate:

$$6H^+ + 5S_2O_3^{2-} \longrightarrow 2S_5O_6^{2-} + 3H_2O$$

With concentrated hydrochloric acid the main products are hydrogen sulfide and hydrogen polysulfide, with no dithionate or sulfate; with less concentrated hydrochloric acid (especially in the presence of arsenious oxide as catalyst) the main product is pentathionate. The polythionic acids are also unstable and decompose by a complex process which has not been elucidated completely.

Thiosulfate solutions are most stable when the pH lies between 9 and 10. A small addition of sodium carbonate to thiosulfate solutions was proposed by Topf and is of value. On the other hand, the indiscriminate addition of alkaline materials to prevent decomposition of thiosulfate solutions is not recommended, since side reactions may take place in the titration of neutral iodine solutions.[77a] In addition, there is evidence that very basic substances are actually detrimental to stability, possibly because of reaction such as:

$$3Na_2S_2O_3 + 6NaOH \longrightarrow 2Na_2S + 4Na_2SO_3 + 3H_2O$$

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[76] Cf. G. Topf, *Z. anal. Chem.*, **26,** 137 (1887); H. I. Waterman, *Chem. Weekblad,* **15,** 1098 (1918); I. M. Kolthoff, *Pharm. Weekblad,* **56,** 878 (1919); *Z. anal. Chem.*, **60,** 344 (1921); F. Feigl, *Ber.*, **56B,** 2086 (1923); F. L. Hahn and H. Windisch, *ibid.*, **55B,** 3163 (1922); A. Skrabal, *Z. anal. Chem.*, **64,** 107 (1924); J. Davidsohn, *Seifensieder-Ztg.*, **52,** 639 (1925); E. Schulek, *Z. anal. Chem.*, **68,** 387 (1926); C. Mayr, *Z. anal. Chem.*, **68,** 274 (1926); C. Mayr and E. Kirschbaum, *ibid.*, **73,** 321 (1928); F. L. Hahn and H. Clos, *ibid.*, **79,** 11 (1929).

[77] O. von Deines, *Z. anorg. Chem.*, **177,** 13 (1928); E. H. Riesenfeld and G. Sydow, *ibid.*, **175,** 49 (1928); J. Scheffer and F. Böhm, *ibid.*, **183,** 151 (1929).

[77a] R. Rands, *Chemistry & Industry,* **1952,** 1001; J. J. Lamond, *ibid.*, 1128.

Mohr showed that sodium thiosulfate in aqueous solution is decomposed by carbonic acid:

$$Na_2S_2O_3 + H_2CO_3 \longrightarrow NaHCO_3 + NaHSO_3 + S$$

Others[78] have found, on the contrary, that carbon dioxide has little effect on the decomposition and that other factors probably contribute to a greater extent to the diminution of the titer.

(*b*) Air-oxidation: Thiosulfate is oxidized slowly by oxygen in air. The reaction takes place in two steps:

$$\begin{array}{lll} Na_2S_2O_3 & \longrightarrow Na_2SO_3 + S & \text{(very slow)} \\ Na_2SO_3 + {}^1/_2O_2 & \longrightarrow Na_2SO_4 & \text{(measurable)} \\ \hline Na_2S_2O_3 + {}^1/_2O_2 & \longrightarrow Na_2SO_4 + S & \end{array}$$

Schulek[79] detected sulfide during the decomposition of thiosulfate and proposed the following reactions to explain this:

$$\begin{array}{rl} Na_2S_2O_3 + H_2O & \longrightarrow Na_2SO_4 + H_2S \\ H_2S + {}^1/_2O_2 & \longrightarrow H_2O + S \\ \hline Na_2S_2O_3 + {}^1/_2O_2 & \longrightarrow Na_2SO_4 + S \end{array}$$

According to him, the decrease in titer of very dilute thiosulfate solutions is best explained by the reaction:

$$2Na_2S_2O_3 + H_2O + {}^1/_2O_2 \longrightarrow Na_2S_4O_6 + 2NaOH$$

An argument in support of the formation of tetrathionate or of the intermediate formation of sulfite is that copper strongly catalyzes the decomposition. It is well known that copper strongly catalyzes the air oxidation of sulfite. Abel,[80] on the other hand, explains the catalytic effect of copper as follows:

$$\begin{array}{lll} 2Cu^{2+} + 2S_2O_3^{2-} & \longrightarrow 2Cu^{+} + S_4O_6^{2-} & \text{(instantaneous)} \\ 2Cu^{+} + {}^1/_2O_2 & \longrightarrow 2Cu^{2+} + O^{2-} & \text{(measurably slow)} \\ O^{2-} + 2H^{+} & \longrightarrow H_2O & \text{(instantaneous)} \\ \hline 2S_2O_3^{2-} + 2H^{+} + {}^1/_2O_2 & \longrightarrow S_4O_6^{2-} + H_2O & \end{array}$$

He attributes the stabilization of thiosulfate solutions by alkaline materials to the precipitation of copper by these substances and, therefore, recommends that thiosulfate solutions be prepared from water distilled in glass and as free as possible of copper. The purity of the water used is very important. Kilpatrick *et al.*[81] found that 0.01*N* thiosulfate solution prepared in ordinary distilled water was 20.6 per cent decomposed in 200 days; in twice-distilled water, 10.9 per cent; in boiled, twice-distilled water, 0.5 per cent; and in twice-distilled water through which carbon dioxide-free air was bubbled, 1.9 per cent.

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[78] G. Topf, *Z. anal. Chem.*, 26, 137 (1887); I. M. Kolthoff, *Pharm. Weekblad*, **56**, 878 (1919); *Z. anal. Chem.*, 60, 344 (1921); I. Bellucci and I. Damiani, *Gazz. chim. ital.*, **64**, 69 (1934); *Chem. Abstr.*, **28**, 4673 (1934).

[79] E. Schulek, *Z. anal. Chem.*, **68**, 387 (1926).

[80] E. Abel, *Ber.*, **56B**, 1076 (1923).

(*c*) Microorganisms: Experiments on the instability of thiosulfate solutions indicate that the chief source of decomposition of standard solutions is the action of microorganisms in the solution.[82] There are apparently microorganisms in air which consume sulfur and remove sulfur from thiosulfate to form sulfite which in turn is oxidized readily to sulfate by air. Several different bacteria are probably present.[83] The metabolic processes of these bacteria probably involve reactions such as:

$$2Na_2S_2O_3 + H_2O + O \longrightarrow Na_2S_4O_6 + 2NaOH$$

and

$$Na_2S_2O_3 \longrightarrow Na_2SO_3 + S$$

$$Na_2SO_3 + O \longrightarrow Na_2SO_4$$

and

$$S + 3O + H_2O \longrightarrow H_2SO_4$$

Perfectly sterile solutions of thiosulfate are practically completely stable; however, if sulfur bacteria are introduced accidentally or purposely, a gradual decomposition takes place.

Bacterial activity is less when the pH of the solution lies between 9 and 10; thus the addition of traces of basic substances is often helpful. Skrabal[84] recommended the addition of a buffer mixture having pH 9.5; Yoshida[85] recommended the addition of borax (0.05*M*) or disodium phosphate (0.1*N*); Mayr and Kirschbaum, and Kolthoff found sodium carbonate (0.001*N*) to be favorable; however, with 0.1*N* sodium carbonate the titer of standard thiosulfate gradually but definitely increases. According to Mayr and to Hahn and

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[81] M. Kilpatrick, Jr., and M. L. Kilpatrick, *J. Am. Chem. Soc.*, **45**, 2132 (1923); F. O. Rice, M. Kilpatrick, Jr., and W. Lemkin, *ibid.*, 1361.

[82] I. M. Kolthoff, *Pharm. Weekblad*, **56**, 878 (1919); *Z. anal. Chem.*, **60**, 344 (1921); C. Mayr, *ibid.*, **68**, 274 (1926); C. Mayr and E. Kirschbaum, *ibid.*, **73**, 321 (1928).

[83] J. S. Joffe, *Sci. Proc. Soc. Am. Bacteriologists*, 1922; *Abstr. Bacteriol.*, **7**, 5 (1923); *Chem. Abstr.*, **17**, 2900 (1923); F. O. Rice, M. Kilpatrick, Jr., and W. Lemkin, *J. Am. Chem. Soc.*, **45**, 1361 (1923); E. Schulek, *Z. anal. Chem.*, **68**, 387 (1926); C. Mayr and E. Kirschbaum, *ibid.*, **73**, 321 (1928).

[84] A. Skrabal, *Z. anal. Chem.*, **64**, 107 (1924).

[85] Y. Yoshida, *J. Chem. Soc. Japan*, **48**, 26 (1927); *Chem. Abstr.*, **21**, 3030 (1927).

Clos,[86] ammonium carbonate should not be used since it accelerates the decomposition by contributing to the growth of sulfur bacteria. Bacterial activity is increased by light; thus thiosulfate solutions should be stored in amber glass bottles in the dark or in diffuse light. The activity is increased also by rising temperature around room temperature. Traces of copper accelerate the rate of decomposition but in certain solutions the copper may have a germicidal property which makes the solution more stable.

Thiosulfate solutions can be preserved by adding disinfectants. Some substances which have been recommended for this purpose are chloroform,[87] mercuric iodide, mercuric cyanide,[88] 1 per cent amyl alcohol,[89] 0.1 per cent sodium benzoate,[90] and carbon disulfide.[85]

Hahn and Clos[86] made a valuable contribution to the clarification of the process of decomposition of thiosulfate solutions. They found that solid sodium thiosulfate ordinarily contains small amounts of pentathionate which decomposes quickly in solution to tetrathionate and sulfur. The following equilibrium exists in solutions and in hydrated crystals of sodium thiosulfate:

$$5S_2O_3^{2-} + 6H^+ \rightleftharpoons 2S_5O_6^{2-} + 3H_2O$$

If the solution is weakly acid, pentathionate forms and decomposes to tetrathionate, reducing the titer of the solution. As mentioned above, thiosulfate can also be air-oxidized to tetrathionate and sulfate, reducing the titer. Very rarely the titer of thiosulfate solutions increases on standing. Hahn and Clos explain this by the formation of sulfite by bacterial action or otherwise; the sulfite in turn reacts with tetrathionate to form thiosulfate and trithionate. The trithioate in weakly alkaline solution hydrolyzes to form sulfate and thiosulfate, and the titer of the solution is increased. Small amounts of alkali tend to suppress the formation of pentathionate, the catalytic action of traces of copper and the formation of sulfite, thus making thiosulfate solutions more stable.

Rue[91] tested the stability of 0.1*N* sodium thiosulfate solutions with

[86] F. L. Hahn and H. Clos, *Z. anal. Chem.*, **79**, 11 (1929).

[87] Cf. J. L. Kassner and E. E. Kassner, *Ind. Eng. Chem., Anal. Ed.*, **12**, 655 (1940).

[88] L. W. Winkler, *Pharm. Zentralhalle*, **69**, 369 (1928); *Chem. Abstr.*, **22**, 3109 (1928).

[89] C. Mayr and E. Kirschbaum, *Z. anal. Chem.*, **73**, 321 (1928).

[90] J. Ehrlich, *Ind. Eng. Chem., Anal. Ed.*, **14**, 406 (1942).

[91] S. O. Rue, *Ind. Eng. Chem., Anal. Ed.*, **14**, 802 (1942).

various additions at 40° C. over a period of 4 months. The maximum variation of untreated solutions during this time was about 0.3–0.4 per cent. Chloroform (1 ml. per liter) and mercuric iodide (10 mg. per liter) were the best of the preservatives tried, but were effective for only about 2 months at this temperature. Sodium hydroxide and sodium carbonate, instead of acting as stabilizers, accelerate the decomposition. All solutions stored at 40° became more acidic on long standing, their normalities decreased and sulfate was formed. These observations are best explained by the reaction:

$$S_2O_3^{2-} + 2O_2 + H_2O \longrightarrow 2SO_4^{2-} + 2H^+$$

Preparation of 0.1N Thiosulfate Solution: Dissolve 24.805 g. of pure sodium thiosulfate pentahydrate in pure, freshly boiled and cooled distilled water. After equalization of the solution temperature, dilute to 1 liter and shake to make uniform. The solution is ready for immediate use.

Because of the instability of standard thiosulfate solutions in the presence of thiobacteria, the preparation should be made under reasonably sterile conditions. Also, one may add 0.01 per cent of sodium carbonate (0.1 g. per liter), a few drops of chloroform or 0.001 per cent of mercuric iodide (10 mg. per liter) as preservatives. If pure salt and good water are used and the solution is kept sterile, it should be stable for several months without the addition of preservatives.[92] However, it is desirable to check the titer of the solution after long use (see Section 9). If the titer decreases by more than 1 per cent, it is well to discard the solution and prepare a fresh one. Once decomposition begins it generally proceeds rapidly. Turbid solutions or those from which sulfur has settled should be discarded and the stock bottle must be cleaned thoroughly and disinfected (hot chromic acid cleaning solution is suitable).

Dilute solutions (0.01N) decompose much more rapidly than 0.1N solutions. The addition of small amounts of preservative to these solutions is recommended. The dilute solutions should be prepared from 0.1N solution and kept no longer than 2 weeks.

Arsenious Acid Solution: The preparation and testing of pure arsenic trioxide and the preparation of standard 0.1N arsenious acid solution are discussed in Chapter II (p. 41).

9. Standardization of Iodine and Thiosulfate Solutions. In the preceding section was discussed the preparation of standard solutions of iodine and thiosulfate by careful weighing of pure reagents. A very simple check on the accuracy of these preparations is obtained by titrating these solutions against one another. However, the titer of these solutions changes in time after long use, and to varying degrees, so that it is necessary to be able to standardize them independently of each other.

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[92] G. M. Johnson, *J. Assoc. Offic. Agr. Chemists*, 25, 659 (1942).

Because special reagents and care are necessary to prepare standard iodine and thiosulfate solutions by direct weighing and because the titers of the solutions change in time, many people prefer to prepare approximate solutions using ordinary reagent chemicals, and then standardize them against primary standard materials. In this way, it is necessary to have available only a small amount of pure primary standard material rather than a large amount of pure iodine and thiosulfate necessary to prepare the standard solutions. Fortunately, several very good primary standard materials are available, and these are discussed below.

PRIMARY SUBSTANCES FOR IODINE STANDARDIZATION

Arsenic Trioxide (As_2O_3; equivalent weight, 49.46; rational, 49.45): The best method for standardizing an iodine solution is against pure arsenic trioxide.[93] The preparation and testing of pure arsenic trioxide are described on p. 41. Pure primary standard arsenic trioxide is available commercially and from the National Bureau of Standards. The iodine-arsenious acid reaction is discussed in Section 5.

Procedure for Standardization: Weigh accurately 0.2 g. of pure dry arsenic trioxide into a 250 ml. Erlenmeyer flask. Dissolve in 10 ml. of *N* sodium hydroxide solution, add 15 ml. of *N* sulfuric acid, and mix thoroughly and cautiously. Then carefully add 1 g. of sodium bicarbonate dissolved in 50 ml. of water and titrate with iodine solution to the first permanent blue tinge, using starch as indicator.

Other Standard Substances. Tartar Emetic ($KSbOC_4H_4O_6 \cdot {}^1/_2H_2O$; equivalent weight, 166.97; rational, 166.92): The salt is purified by recrystallization from water. When dried in air, the salt retains $^1/_2$ mole of water but is anhydrous when dried at 100°C. In either form it may be used as a primary standard and has been recommended by several authors.[94] The titration procedure is exactly like that for arsenic trioxide in the presence of excess bicarbonate. The speed of the reaction near the end of the titration is slow, so that salt is not so suitable a standard as arsenic trioxide.

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[93] R. M. Chapin, *J. Am. Chem. Soc.*, 41, 351 (1919).

[94] Cf. S. W. Young, *J. Am. Chem. Soc.*, 26, 1028 (1904); S. Metzl, *Z. anorg. Chem.*, 48, 156 (1906); O. Lutz, *ibid.*, 49, 338 (1906).

Sodium Thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$; equivalent weight, 248.21; rational, 248.05): The purification and testing of sodium thiosulfate are discussed on p. 224; and standardization of iodine solution with this reagent presents no difficulties; the salt is weighed, dissolved in water, and titrated with iodine solution. A slight uncertainty regarding water content arises from the possible occlusion of water by the salt. Young,[95] therefore, advised the use of anhydrous sodium thiosulfate as a standard substance. Tomlinson and Ciapetta[96] also recommend the anhydrous salt. A sample of C.P. sodium thiosulfate pentahydrate is dried at 120° to constant weight and stored over calcium chloride. The time of drying depends upon the frequency of stirring the solution formed upon heating the hydrated salt and later upon the frequency and degree of subdivision. [Possibly a more effective method for obtaining the anhydrous salt would be to dehydrate the pentahydrate in a vacuum desiccator at room temperature followed by heating the powder to constant weight at 120°. Authors.] The anhydrous salt is stable even when exposed to light and air, is not excessively hygroscopic and is redried readily at 120°. The equivalent weight of the anhydrous salt is 158.13; rational, 158.07.

Barium Thiosulfate Monohydrate (~~$BaSO_4$~~ BaS_2O_3 $\cdot H_2O$; equivalent weight, 267.51; rational, 267.45): Plimpton and Chorley[97] first suggested the use of barium thiosulfate and barium thiosulfate monohydrate as primary standards for iodine solutions. More recently, MacNevin and Kriege[97a] thoroughly investigated the use of the monohydrate and found it an excellent primary standard material. Barium thiosulfate monohydrate is prepared readily by mixing aqueous solutions of barium chloride and sodium thiosulfate, filtering off the precipitate on a medium-porosity sintered-glass funnel with suction, washing successively with distilled water, 95 per cent ethanol and diethyl ether, and finally drying and storing the crystals under ordinary atmospheric temperature and humidity. Solid having a purity of 99.85 per cent is obtained. The monohydrate is perfectly stable up to 50°C.; between 50° and 100°C. a large loss in weight occurs from dehydration of the salt; above 100° further losses occur from decomposition of the thiosulfate. The anhydrous salt, while it can be obtained in the pure form, is not suitable as a standard substance because of the slowness of dissolving in water. Barium thiosulfate monohydrate has a limited solubility in water but dissolves so rapidly that this does not interfere with its use in iodometric standardizations; indeed, the disappearance of the solid can be used as an indication of the approach of the end-point.

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[95] S. W. Young, *J. Am. Chem. Soc.*, 26, 1028 (1904).

[96] H. M. Tomlinson and F. G. Ciapetta, *Ind. Eng. Chem., Anal. Ed.*, 13, 539 (1941).

[97] R. T. Plimpton and J. C. Chorley, *J. Chem. Soc.*, **67**, 314 (1895); cf. also M. Mutnianski, *Z. anal. Chem.*, 36, 220 (1897).

[97a] W. M. MacNevin and O. H. Kriege, *Anal. Chem.*, **25**, 767 (1953).

Hydrazine Sulfate ($N_2H_4 \cdot H_2SO_4$; equivalent weight, 32.53; rational, 32.51): Hydrazine sulfate is obtained pure by repeated recrystallization from water and drying at 100°C. It has been mentioned as a standard substance by several investigators.[98] In the presence of much bicarbonate, hydrazine reacts with iodine:

$$N_2H_4 + 2I_2 \longrightarrow N_2 + 4HI$$

Kolthoff observed that the last drops of iodine are decolorized only slowly; one must titrate until the iodine color persists for at least 2 minutes. Starch delays the reaction appreciably and is better avoided. Cattelain recommended that a slight excess of iodine be added and back-titrated with thiosulfate. Such an indirect method is in principle not to be recommended for standardization.

Sodium Acetomercurithymol Sulfonate: Bordeianu, Petrescu, and Staicovici[99] state that this substance is obtained easily in a pure state. It has a high molecular weight and reacts with iodine with displacement of the acetomercuric group. The end-point is found with starch. It is claimed that the results are more accurate than those obtained with arsenic trioxide as standard. Fuller details are not given in the quoted abstract.

Potassium Chlorostannite ($K_2SnCl_4 \cdot 2H_2O$; equivalent weight, 187.38): As already discussed on p. 58, this salt is recommended for the standardization of permanganate and iodine solutions.[100] Its preparation and properties are described on p. 58. A great disadvantage of this standard substance is its sensitivity to air-oxidation.

Procedure for Standardization: To 200 ml. of hot water add 2 g. of sodium bicarbonate and 20 ml. of concentrated hydrochloric acid to provide a carbon dioxide atmosphere. Add a weighed amount of pure potassium chlorostannite, and titrate with iodine solution using starch as indicator.

Standard Sodium Hydroxide: Hahn[101] recommends the use of the reaction

$$SO_3^{2-} + H_2O + I_2 \longrightarrow SO_4^{2-} + 2H^+ + 2I^-$$

as a check on the titer of an iodine solution with standard sodium hydroxide. A solution of pure sodium or potassium sulfite is prepared which is slightly alkaline to thymolphthalein. A measured volume of iodine solution is added, and the acid formed by the reaction is titrated with standard sodium hydroxide solution, using phenolphthalein or thymolphthalein as indicator.

Other Standards: Kalmann[102] proposed *sodium sulfite* as a standard substance, but it is not suitable. The *gas-volumetric* standardization proposed by Baumann,[103] whereby the iodine solution is treated with peroxide and potassium hydroxide and the volume of liberated oxygen gas is measured, has no advantages.

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[98] R. Stollé, *J. prakt. Chem.*, (2) **66**, 332 (1902); I. M. Kolthoff, *J. Am. Chem. Soc.*, **46**, 2009 (1924); E. Cattelain, *J. pharm. chim.*, (8) **2**, 387 (1925); *Ann. fals. et fraudes*, **19**, 145 (1926).

[99] C. V. Bordeianu, I. N. Petrescu, and I. Staicovici, *Bul. Soc. Stiinte Farm. România*, **4**, 473 (1939); *Chem. Abstr.*, **34**, 4356 (1940).

[100] T. Karantassis and L. Capatos, *Compt. rend.*, **194**, 1938 (1932).

[101] F. L. Hahn, *Ind. Eng. Chem., Anal. Ed.*, **14**, 773 (1942).

[102] W. Kalmann, *Ber.*, **20**, 568 (1887).

[103] A. Baumann, *Z. angew. Chem.*, **4**, 203 (1891).

PRIMARY SUBSTANCES FOR THIOSULFATE STANDARDIZATION

Iodine (equivalent weight, 126.91; rational, 126.89): The preparation and use of pure iodine have been described, p. 220. The best method of weighing pure iodine without loss is probably that suggested by Treadwell:[104]

> Place 2–2.5 g. of pure potassium iodide and 0.5 ml. of water in a glass-stoppered weighing bottle; stopper the bottle and weigh accurately after the temperature has reached equilibrium. Introduce quickly, and without loss of solution, 0.3–0.4 g. of pure iodine and restopper. The iodine dissolves quickly in the potassium iodide solution. After equilibration of temperatures reweigh the bottle; the difference in weights is the weight of pure iodine, Dilute the solution and transfer it quickly and quantitatively to a 250 ml. Erlenmeyer flask or, better, place the closed weighing bottle into the flask containing about 100 ml. of water and 1 g. of potassium iodide and then remove the stopper. Titrate the iodine solution in the flask with thiosulfate solution, adding starch near the end-point.

Iodine Cyanide (ICN; equivalent weight, 76.46; rational, 76.45): Iodine cyanide is easily obtained pure, and Kolthoff[105] has tested its use as a standard substance. Iodine is mixed thoroughly in a mortar with a slight excess of mercuric cyanide and the mixture is exposed to direct sunlight for several days. The mass then becomes red-brown from the mercuric iodide which separates. The iodine cyanide is then sublimed on a 40° water bath. *Care must be taken since the substance is very poisonous.* Loss by volatilization during weighing is negligible. Iodine cyanide dissolves only slowly in water; hence it is first dissolved in alcohol. Water is added, the solution is transferred quantitatively to an Erlenmeyer flask, heated with potassium iodide and acid, and the liberated iodine:

$$2ICN + 2HI \rightleftharpoons 2HCN + 2I_2$$

is titrated with thiosulfate. The removal of iodine from the solution by thiosulfate displaces the equilibrium quantitatively to the right.

Potassium Iodate (KIO_3; equivalent weight, 35.67; rational, 35.66): Pure potassium iodate may be obtained commercially and used without further purification except for drying. It may be prepared otherwise by several recrystallizations of technical material from water followed by drying at 150–180° C. The salt is anhydrous and may be kept without danger of absorbing moisture. It is an excellent standard substance except for its small equivalent weight. This disadvantage may be circumvented by preparing a large volume of standard iodate solution and using aliquot portions for the standardization of thiosulfate. For the standardization, iodate is reacted with iodide in acid solution:

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[104] F. P. Treadwell and W. T. Hall, *Analytical Chemistry*, 9th ed., Vol. II, Wiley, New York, 1942, p. 588.

[105] I. M. Kolthoff, *Z. anal. Chem.*, 59, 411 (1920).

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

The reaction is quantitative with only a slight excess of acid; thus the error due to air-oxidation of iodide is negligible. The iodine, quantitatively liberated by iodate, is titrated with thiosulfate solution.

Milstead[106] reported that a sample of analytical grade potassium iodate obtained commercially liberated too much iodine. After being twice recrystallized from water, the product was worse. It was suspected that the original product contained sodium iodate [or possibly bromate, calcium iodate, or potassium hydrogen iodate; Authors], but this has not been ascertained.

Procedure for Standardization: Weigh 0.12–0.17 g. of pure potassium iodate into a 250 ml. Erlenmeyer flask and dissolve in 25 ml. of water. Add 2 g. of potassium iodide (iodate free) and shake until dissolved. Add 10 ml. of *N* hydrochloric acid and titrate immediately with thiosulfate solution, adding starch near the end-point.

Note: Iodine should be liberated only after sufficient iodide is present in the solution to minimize the loss of iodine by volatilization. This is accomplished by adding either the acid or the iodate just before titrating with thiosulfate.

Potassium Hydrogen Iodate ($KH(IO_3)_2$; equivalent weight, 32.50; rational, 32.49): The preparation of pure potassium hydrogen iodate and the literature regarding its use as a standard substance have been discussed in Vol. II, p. 100. According to Kolthoff and van Berk,[107] this substance is useful for many volumetric standardizations but offers no advantage over potassium iodate for the standardization of thiosulfate. The standardization is carried out in a manner similar to that using potassium iodate; however, it is best to add the potassium hydrogen iodate to the acidified iodide solution.

Riegler[108] suggested the use of pure iodic acid as a standard substance. According to him, iodic acid reacts with thiosulfate:

$$6Na_2S_2O_3 + 6HIO_3 \longrightarrow 3Na_2S_4O_6 + 5NaIO_3 + NaI + 3H_2O$$

However, this reaction is too indefinite to use for standardizing thiosulfate solutions and is not recommended.[109]

Potassium Bromate ($KBrO_3$; equivalent weight, 27.836; rational, 27.83): Potassium bromate is obtained pure by recrystallizing from water and drying at 180°C.[110] Bromate reacts with iodide in the presence of acid:

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[106] K. L. Milstead, *J. Assoc. Offic. Agr. Chemists*, 22, 567 (1939).

[107] I. M. Kolthoff and L. H. van Berk, *J. Am. Chem. Soc.*, 48, 2799 (1926).

[108] E. Riegler, *Chem. Zentr.*, 1897, II, 1169.

[109] C. F. Walker, *Am. J. Sci.*, 4, 235 (1897).

$$BrO_3^- + 6I^- + 6H^+ \longrightarrow Br^- + 3I_2 + 3H_2O$$

and the liberated iodine is titrated with thiosulfate. The reaction of bromate with iodide and acid is not so rapid as that of iodate. If the titration with thiosulfate is made immediately after acidification and if the hydrogen-ion concentration is low, free bromic acid may remain unreacted and oxidize thiosulfate to sulfate during the titration.

Tests of the Purity of Potassium Bromate. Halide: The presence of a trace of bromide may be detected in two ways:

(*a*) With Silver Nitrate: Since silver bromate is itself slightly soluble, the test must not be made on a concentrated bromate solution. Add 1 drop of 0.1N silver nitrate to 5 ml. of 1 per cent bromate solution; no opalescence or turbidity should appear. Sensitivity, 0.02 per cent KBr or KCl.

(*b*) With Sulfuric Acid: Bromate reacts with bromide in acid solution to form free bromine. Acidify 5 ml. of 1 per cent bromate solution with 2 ml. of 4N sulfuric acid and allow to stand 5 minutes; the solution should not appear yellow. Sensitivity, 0.01 per cent KBr. The test may be made more sensitive by adding 1 drop of 0.1 per cent methyl orange in water to the acidified solution. The red color of the indicator should not disappear in 2 minutes. Sensitivity, 0.004 per cent KBr.

Water: Dry 10 g. of potassium bromate at 100°; the salt should not lose more than 1 mg.

Procedure for Standardization: To a 250 ml. Erlenmeyer flask, add 25 ml. of 0.1N standard potassium bromate solution, 5 ml. of N potassium iodide, and at least 5 ml. of 4N hydrochloric or 10 ml. of 4N sulfuric acid. Stir the solution well and titrate with the thiosulfate solution.

Sodium Bromate: According to Kratschmer,[111] this substance can be prepared pure in the same way as pure potassium bromate described above. It can be used as a primary standard substance but is not recommended because of its very small equivalent weight.

Potassium Chlorate: This has also been suggested as a standard substance[112] but is not to be recommended for the purpose.

Potassium Ferricyanide ($K_3Fe(CN)_6$, equivalent weight, 329.26; rational, 329.15): Potassium ferricyanide was recommended as a standard substance by Kolthoff.[113] It is easily obtained pure by repeated recrystallization from water and drying at 100°C. Its large equivalent weight (almost 10 times that of potassium iodate) is of great practical value. The titer of a thiosulfate solution against potassium ferricyanide agrees to within 0.1 per cent with that determined against potassium iodate.

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[110] H. C. Van Dame, *J. Assoc. Offic. Agr. Chemists*, **30**, 502 (1947).

[111] Kratschmer, *Z. anal. Chem.*, **24**, 546 (1885).

[112] H. Ditz and B. M. Margosches, *Z. angew. Chem.*, **16**, 317 (1903); **18**, 1516 (1905); cf. also, A. Kolb and E. Davidson, *ibid.*, **17**, 1883 (1904).

[113] I. M. Kolthoff, *Pharm. Weekblad*, **59**, 66 (1922).

Procedure for Standardization: Weigh a 1 g. sample of pure potassium ferricyanide into a glass-stoppered Erlenmeyer flask. Add 30 ml. of water and 10 ml. of *N* potassium iodide and mix well. Add 20 ml. of 4*N* hydrochloric acid, stopper the flask, and let it stand for one minute. Add 10 ml. of 30 per cent zinc sulfate solution; a thick gelatinous precipitate forms. Titrate with thiosulfate, adding starch near the end of the titration, and titrate to the disappearance of the blue color. If the reagents used are free of iron the potassium zinc ferrocyanide is pure white at the end-point.

Potassium Dichromate ($K_2Cr_2O_7$; equivalent weight, 49.04; rational, 49.03): Dichromate reacts with iodide in acid solution according to the equation:

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 3I_2 + 2Cr^{3+} + 7H_2O$$

There are many references in the literature to the reliability of potassium dichromate as a primary standard utilizing this reaction. The first such reference was made by Zulkowsky.[114]

It is recognized that, under certain conditions, dichromate uses too much thiosulfate in the standardization. Wagner[115] found an excess consumption of 0.3–0.4 per cent. He attributes this excess to an air-oxidation of hydriodic acid induced by the dichromate-hydriodic acid reaction. The effect is greater, the slower the reaction between dichromate and hydriodic acid; thus, varying results are obtained by varying the experimental conditions. These observations of Wagner have been confirmed by others.[116]

In opposition, Bruhns[117] published the results of his investigation of the subject. On the basis of these, the reaction scarcely utilizes excess thiosulfate and the air-oxidation of hydriodic acid is negligible. In agreement with Bruhns, Kolthoff[118] showed that potassium dichromate is a satisfactory standard substance if used under proper experimental conditions. Important factors are the acid and iodide concentrations and the time for complete reaction of dichromate with iodide. The acidity of the solution is of great importance; if it is sufficiently high, correct and reproducible titrations are always obtained. However, the acidity should not be so high that air-oxidation of iodide becomes appreciable. For best results, the hydrogen-ion concentration should be around 0.2–0.4*M*. The potassium iodide concentration should be at least 2 per cent to ensure complete and stoichiometric reaction with dichromate and to prevent the loss of iodine. The reaction mixture should be allowed to stand in the dark for 10–15 minutes before being titrated with thiosulfate.

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[114] H. Zulkowsky, *J. prakt. Chem.*, **103**, 362 (1868).

[115] J. Wagner, *Z. anal. Chem.*, **38**, 1454 (1899).

[116] Cf. O. Meindl, *Z. anal. Chem.*, **58**, 529 (1919); C. R. McCrosky, *J. Am. Chem. Soc.*, **40**, 1662 (1918); W. C. Vosburgh, *ibid.*, **44**, 2120(1922); G. Jander and H. Beste, *Z. anorg. u. allgem. Chem.*, **133**, 73 (1924); W. C. Bray and H. E. Miller, *J. Am. Chem. Soc.*, **46**, 2204 (1924); K. Böttger and W. Böttger, *Z. anal. Chem.*, **69**, 145 (1926).

[117] G. Bruhns, *J. prakt. Chem.* [N.S.], **93**, 73, 312 (1916); **95**, 37 (1917); *Z. anorg. u. allgem. Chem.*, **49**, 277 (1916).

[118] I. M. Kolthoff, *Z. anal. Chem.*, **59**, 401 (1920); cf. also S. Popoff and J. L. Whitman, *J. Am. Chem. Soc.*, **47**, 2259 (1925); F. L. Hahn, *ibid.*, **57**, 614 (1935); S. O. Rue, *Ind. Eng. Chem., Anal. Ed.*, **14**, 802 (1942).

An important contribution to the understanding of the discordant reports regarding the accuracy of the standardization of thiosulfate solutions against potassium dichromate was made by Hahn.[119] He found that chromium(III) under certain conditions forms a stable complex with thiosulfate which reacts only very slowly with iodine. Chromic salts do not form the complex with thiosulfate when the two are mixed; however, if dichromate is reduced in the presence of thiosulfate, the complex is formed. Therefore, if dichromate reacts with iodide in weakly acid solution and the liberated iodine is titrated with thiosulfate before all the dichromate is reduced, an excess of thiosulfate is required. Hahn was able to show the presence of thiosulfate in solutions containing excess iodine if the conditions were favorable for complex formation. He also showed that accurate results are obtained if sufficient time is allowed for the complex to react with iodine, or if the dichromate is completely reduced before the liberated iodine is titrated with thiosulfate so that the complex is not formed. In strong acid solutions, the rate of reaction between chromate and iodide is so fast that the oxidant is completely reduced before the addition of thiosulfate and no errors are introduced.

Preparation and Testing of Pure Potassium Dichromate: These have been described fully in Chapter V (p. 176). Very pure potassium dichromate in available commercially[120] and from the National Bureau of Standards.

Procedure for Standardization: Add to a glass-stoppered Erlenmeyer flask 100 ml. of a solution containing 2 g. of potassium iodide and 20 ml. of

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[119] F. L. Hahn, *J. Am. Chem. Soc.*, **57**, 614 (1935); *Z. anal. Chem.*, **97**, 305 (1934).

[120] G. McClellan, *J. Assoc. Offic. Agr. Chemists*, **32**, 587 (1949).

N hydrochloric or sulfuric acid. Accurately weigh 0.2–0.23 g. of pure potassium dichromate (dried at 200°) into this flask, stopper the flask, mix thoroughly, and allow to stand in the dark for 10 minutes. Titrate with thiosulfate solution, adding starch as indicator near the end-point. The color changes sharply from blue to light green.

When the standardization of thiosulfate is carried out at high summer temperatures (30–40°C.), Rue[121] found the results by the above procedure to be unreliable. He recommends the following procedure, which also yields good results at lower temperatures.

Procedure: Weigh 0.2–0.22 g. of pure potassium dichromate into a 500 ml. glass-stoppered Erlenmeyer flask. Wash down the sides of the flask with water and dilute to 125 ml. Add 5 g. of potassium iodide. After dissolution of the iodide, add 5 ml. of $6N$ hydrochloric acid with constant swirling. Carefully rinse the sides of the flask so that a layer of water remains above the solution, stopper the flask, and place in the dark for about 6 minutes. Add 165 ml. of water and titrate with the thiosulfate solution, adding starch near the end-point.

Sully[122] found that cupric copper in weakly acid solution greatly accelerates the reaction between dichromate and iodide. In order to avoid air-oxidation of iodide, he recommends the use of acetic acid, instead of hydrochloric acid, with a trace of copper present to reduce the reaction time.

Procedure: To 20 ml. of $0.1N$ dichromate solution, add 5 ml. of glacial acetic acid, 5 ml. of $0.001M$ copper sulfate, 20 ml. of water, and 20 ml. of 15 per cent potassium iodide solution. Titrate the solution with thiosulfate at about 20° (not over 25° to avoid air-oxidation). Complete the titration in about 3–4 minutes after the addition of potassium iodide. The end-point is stable. A correction of 0.05 ml. of $0.1N$ thiosulfate is applied for the amount of copper added. [This correction probably can be avoided if cuprous iodide suspension is used as catalyst. Authors].

Potassium Permanganate: The standardization of thiosulfate against potassium permanganate was suggested first by Volhard.[123] Since then the method has been studied and recommended by many investigators.[124] The titration is simple and exact but, since the permanganate solution must first be standardized against a standard substance, this leads to a secondary standardization of thiosulfate. Potassium permanganate is, therefore, not recommended as a standard substance, especially since there are available so many good primary standard substances for direct standardization of thiosulfate solutions. The titration is useful as a check of one solution against the other because of its exactness.

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[121] S. O. Rue, *Ind. Eng. Chem., Anal. Ed.*, 14, 802 (1942).

[122] B. D. Sully, *J. Chem. Soc.*, **1942**, 366.

[123] J. Volhard, *Ann.*, **198**, 333 (1879).

[124] T. Milobendzki, *Z. anal. Chem.*, 46, 18 (1907); W. C. Bray and G. M McKay, *J. Am. Chem. Soc.*, **32**, 1193 (1910); W. C. Vosburgh, *ibid.*, **44**, 2120 (1922); S. Popoff and F. L. Chambers, *ibid.*, **45**, 1358 (1923); J. M. Hendel, *Z. anal. Chem.*, **63**, 321 (1923); W. C. Bray and H. E. Miller, *J. Am. Chem. Soc.* **46**, 2204 (1924); S. Popoff and J. L. Whitman, *ibid.*, **47**, 2259 (1925); S. Popoff and A. H. Kunz, *ibid.*, **51**, 1307 (1929).

Add to a definite volume of potassium permanganate solution some acid and potassium iodide solution (at least 6 per cent potassium iodide and about $0.1M$ in hydrochloric or sulfuric acid). Titrate the liberated iodine with thiosulfate.

Potassium Peroxydisulfate ($K_2S_2O_8$; equivalent weight, 135.17; rational, 135.09): King and Jette[125] suggest potassium peroxydisulfate as a standard substance. The pure salt is obtained by recrystallizing from water between 50° and 0°C. and drying in a vacuum desiccator over sulfuric acid.

In neutral solution, especially in the presence of potassium chloride, peroxydisulfate reacts with iodide to liberate an equivalent amount of iodine:

$$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$$

which is titrated with thiosulfate solution. The time required for the complete reaction of peroxydisulfate depends on the iodide concentration and on the ionic strength.[126]

Copper (equivalent weight, 63.54; rational, 63.54): The method of Gooch and Heath[127] for standardizing sodium thiosulfate solution against copper dissolved in nitric acid was investigated by Popoff *et al.*[128] Cupric copper is reduced by iodide:

$$2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$$

and the liberated iodine is titrated with thiosulfate solution. Nitrous acid, formed by the reaction of copper with nitric acid, also liberates iodine and must be eliminated before iodide is added. The cuprous iodide precipitate tends to adsorb some iodine which impairs the sharpness of the titration end-point and introduces some error. Foote and Vance[129] improved the situation by adding a soluble thiocyanate near the end-point of the thiosulfate titration. Cuprous thiocyanate is less soluble than cuprous iodide and has less tendency to adsorb iodine; thus the surface of the precipitate is transformed to cuprous thiocyanate and iodine is not retained by the precipitate.

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[125] C. V. King and E. Jette, *J. Am. Chem. Soc.*, 52, 608 (1930).

[126] Cf. A. von Kiss and V. Bruckner, *Z. physik. Chem.*, **128,** 71 (1927); A. Schwicker, *Z. anal. Chem.*, **74,** 433 (1928); A. Kurtenacker and H. Kubina, *ibid.*, **83,** 14 (1930).

[127] F. A. Gooch and F. H. Heath, *Z. anorg. Chem.*, 55, 119 (1907); *Am. J. Sci.*, (4) 24, 65 (1907).

[128] S. Popoff, M. Jones, C. Rucker, and W. W. Becker, *J. Am. Chem. Soc.*, 51, 1299 (1929).

[129] H. W. Foote and J. E. Vance, *J. Am. Chem. Soc.*, 57, 845 (1935).

Procedure for Standardization: Dissolve a weighed amount of electrolytic copper (about 0.25 g.) in 8 ml. of 6*N* nitric acid and evaporate the solution on a steam bath until on cooling it completely solidifies. Dissolve the solid in about 20 ml. of water and add dilute sodium hydroxide solution until a permanent precipitate forms. Add 8*M* acetic acid until the precipitate just dissolves and add 4 drops in excess. Dilute the solution to 100 ml., add potassium iodide so that 4 per cent of potassium iodide is present at the end-point, and titrate with thiosulfate solution. Near the end-point, add 2–3 g. of ammonium thiocyanate and starch indicator solution and complete the titration.

Foote[130] recommended the removal of nitric and nitrous acids from the solution by evaporating with sulfuric acid, adding hydrochloric acid and again evaporating to fumes of sulfuric acid. Nitrous acid and lower oxides of nitrogen can be eliminated, avoiding the long evaporation procedure, by reducing with urea[131] or with sulfamic acid.[132]

Procedure: Dissolve the sample of pure copper in dilute nitric acid. Neutralize the solution with 4*N* sodium hydroxide until a precipitate forms; then add 6*N* acetic acid until the copper hydroxide just dissolves. Add sulfamic acid to reduce nitrous acid and then add potassium iodide. Titrate the liberated iodine, adding ammonium thiocyanate and starch near the end-point.

To avoid the interference of nitric acid, Kolb[133] dissolved a weighed sample of pure copper by boiling gently with concentrated perchloric acid (about 11*M*). The solution is allowed to cool slightly, diluted with an equal volume of water, and boiled 2 minutes to drive off any chlorine which may be present. After the solution is cool, potassium iodide is added and the iodine titrated with thiosulfate solution.

Copper Sulfate ($CuSO_4 \cdot 5H_2O$; equivalent weight, 249.69; rational 249.56): Schoorl[134] recommends this salt as a standard substance.

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[130] H. W. Foote, *J. Am. Chem. Soc.*, **60**, 1349 (1938).

[131] L. O. Hill, *Ind. Eng. Chem., Anal. Ed.*, **8**, 200 (1936); cf. H. Koelsch, *Chem. Ztg.*, **37**, 753 (1913).

[132] R. C. Brasted, *Anal. Chem.*, **24**, 1040 (1952).

[133] J. J. Kolb, *Ind. Eng. Chem., Anal. Ed.*, **11**, 197 (1939).

[134] N. Schoorl, *Pharm. Weekblad*, **76**, 1441 (1939).

It is obtained in a pure state by recrystallization and is dried readily since the hydrate is stable if the relative humidity is between 0.31 and 0.97. In this respect, the pentahydrate is preferable to the monohydrate suggested by Foote[135] as this salt is transformed to the trihydrate at a relative humidity of 0.20 and to the pentahydrate at relative humidity of 0.31. Copper sulfate crystals obtained in the ordinary way may contain an excess of water. According to Schoorl, the excess of water is removed by drying the salt for 24 hours at 105°C. (transformation to monohydrate suggested by Foote) and the pentahydrate is regenerated by keeping the monohydrate in a hygrostat at a relative humidity between 0.32 and 0.94. The regeneration is complete in 1–2 days. For the standardization, Schoorl recommended the procedure proposed by Foote.

Procedure for Standardization: Dissolve about 1 g. of pure copper sulfate pentahydrate in 20 ml. of water. Add 5 ml. of 4*N* acetic acid and 1.5 g. of potassium iodide. Titrate with thiosulfate and add, toward the end, 5 ml. of 1 per cent starch solution. When the blue color has disappeared, add 5 ml. of 20 per cent potassium or ammonium thiocyanate, and continue the titration slowly until the blue color (which reappears on addition of thiocyanate) just disappears.

Other compounds of copper which have been recommended are the double salt of ammonium copper chloride ($(NH_4)_2CuCl_4 \cdot 2H_2O$)[135a] and cupric oxide.[135b]

Oxalic Acid ($H_2C_2O_4 \cdot 2H_2O$; equivalent weight, 63.03; rational 63.00): The preparation and tests of purity of oxalic acid have been described in Vol. II, p. 95.

The fundamental reaction involved in the standardization of thiosulfate solution against oxalic acid is the interaction of hydrogen, iodide, and iodate ions to form free iodine:

$$6H^+ + 5I^- + IO_3^- \longrightarrow 3I_2 + 3H_2O$$

The second ionization constant of oxalic acid is so small that both hydrogen ions do not react quantitatively. As has been discussed in Vol. II, p. 97, the addition of enough calcium or magnesium salt of a strong acid makes oxalic acid behave as a stronger acid by forming a precipitate or complex with oxalate ion and the liberation of iodine is quantitative. It is, of course, necessary that the salts used in the standardization contain no acid or basic impurities.

Procedure for Standardization: Dissolve a weighed sample of pure oxalic acid in water. For every 50 ml. of 0.1*N* oxalic acid, add 12.5 ml. of 0.1*M* magnesium chloride, 10 ml. of *N* potassium iodide and 10 ml. of 3 per cent potassium iodate solution. Titrate the liberated iodine with thiosulfate, adding starch near the end-point.

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[135] H. W. Foote, *J. Am. Chem. Soc.*, 60, 1349 (1938).

[135a] G. Vavrinecz, *Magyar Kém. Folyóirat*, 42, 1 (1936).

[135b] L. Rosenthaler, *Pharm. Acta Helv.*, 28, 308 (1953)

o-Chlorobenzoic Acid ($Cl.C_6H_4.COOH$; equivalent weight, 156.57): Murgulescu and Latiu[136] dissolve 0.5 g. of the acid in 10 ml. of alcohol, add 7 ml. of *N* potassium iodide solution and 7 ml. of 3 per cent potassium iodate solution. The iodine liberated is titrated with thiosulfate.

Sulfamic Acid (NH_2SO_3H; equivalent weight, 97.09; rational, 97.03): Sulfamic acid has been recommended as a standard substance in alkalimetry (for a discussion, see Vol. II, p. 99). Since it is a strong acid in aqueous solution, it should be superior to oxalic acid as a standard substance for the standardization of thiosulfate solutions.

Cyanogen Bromide (BrCN; equivalent weight, 52.97): Pure cyanogen bromide is prepared from an alkali cyanide and bromine by the method of Scholl[137] and obtained anhydrous by distillation from calcium chloride and metallic sodium according to Steinkopf.[138] Møller[139] recommended cyanogen bromide, which is fairly stable in dry air and stable for a year in a sealed ampoule, as a universal standard substance. However, its properties (e.g., stability, volatility during weighing, purity) have not been studied sufficiently and a thorough investigation is necessary before cyanogen bromide can be generally used.

The fundamental reaction involved in the standardization of thiosulfate is:

$$BrCN + 2I^- + H^+ \longrightarrow Br^- + HCN + I_2$$

Cyanogen bromide reacts with hydroxyl ion:

$$BrCN + 2OH^- \longrightarrow Br^- + OCN^- + H_2O$$

On acidification, the cyanic acid decomposes readily to carbon dioxide and ammonia. The latter is distilled from alkaline solution and used to standardize acids. From a practical point of view, this procedure cannot be recommended.

For the standardization of silver nitrate solution, the cyanogen bromide is converted to bromide and cyanate in alkaline solution, which is then acidified and the bromide titrated with silver nitrate solution.

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[136] I. G. Murgulescu and E. Latiu, *Z. anal. Chem.*, 125, 267 (1943).

[137] R. Scholl, *Ber.*, 29, 1822 (1896); F. Baum, *ibid.*, 41, 523 (1908).

[138] W. Steinkopf, *J. prakt. Chem.* [N. S.] 109, 347 (1925).

[139] M. Møller, *Z. anal. Chem.*, 99, 351 (1934); *Kgl. Danske Videnskab. Selskab Mat.-fys. Medd.*, 12, No. 17, 18 pp. (1934); *Chem. Abstr.*, 29, 2825 (1935).

CHAPTER VII

IODOMETRIC DETERMINATION OF INORGANIC SUBSTANCES

1. Halogens and Their Compounds.

FREE HALOGENS

Iodine: Free iodine is determined by a procedure similar to that used to standardize thiosulfate solution against pure iodine (p. 234). A weighed amount of sample is dissolved in potassium iodide solution and titrated with standard thiosulfate solution. The iodide increases the solubility of iodine in water and reduces its volatility. Iodide is necessary also to prevent side reactions between iodine and thiosulfate; iodine, in the absence of iodide, is a stronger oxidizing agent and partially oxidizes thiosulfate to sulfate. If iodine is in alcoholic solution free of iodide (e.g., in a tincture), iodide must be added to the solution before it is titrated with thiosulfate.

Iodometric methods were first placed on a sound basis by Bunsen[1] who titrated iodine with a solution of sulfurous acid. This reaction was first investigated by Du Pasquier,[2] but it remained for Bunsen to eliminate the sources of error. He applied the titration to the determination of chlorine, bromine, hydrogen sulfide, and of several oxidizing agents. Schwarz[3] recommended the use of sodium thiosulfate in place of sulfurous acid; his recommendation eventually became adopted universally.

Bromine and Chlorine: These halogens cannot be titrated directly with thiosulfate since they oxidize the latter partially to tetrathionate and partially to sulfate. The free halogens are treated with excess of potassium iodide and the iodine liberated is titrated with thiosulfate solution. Bromine and chlorine in aqueous solution are very volatile; it is best to determine them by adding some potassium iodide to a glass-stoppered flask, taring, adding a suitable amount of sample, weighing, and finally titrating with standard thiosulfate solution.

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[1] R. Bunsen, *Ann.*, 86, 265 (1853).

[2] A. Du Pasquier, *Ann. chim. et. phys.*, (2) 73, 310 (1840).

[3] H. Schwarz, *Praktische Anleitung zu Massanalysen*, Vieweg, Braunschweig, 1853; cf. H. Rose in *Handbuch der anal. Chem.*, 6th ed., R. Finkener, ed., Vol. 2, p. 937.

For the iodometric titration of traces of chlorine in water and the effect of manganese dioxide at varying pH and iodide-ion concentration, reference is made to a critical study by Hallinan and Thompson.[4]

Iodine and Bromine in the Presence of One Another: Formic acid and formate ion are not oxidized by iodine but are oxidized readily by bromine:

$$HCOOH + Br_2 \longrightarrow CO_2 + 2HBr$$

Spitzer[5] utilized this difference to determine iodine and bromine in the presence of one another. The iodine is determined by adding sodium formate to a portion of sample and titrating with thiosulfate after the bromine is reduced. The sum of iodine and bromine is determined on another portion of sample. The accuracy of the determination is not affected by pH variations between 3.0 and 6.9 nor by large excesses of sodium formate.

Procedure: Weigh about 0.3 g. of sample into a 250 ml. volumetric flask and dilute to volume with 25 per cent potassium bromide solution. Pipette 25 ml. aliquot portions into each of two flasks and dilute each to about 100 ml. with water. To one add 1–1.5 ml. of 5 per cent sodium formate solution, shake vigorously, and allow to stand for 10 minutes. Titrate with standard sodium thiosulfate solution, using starch as indicator. To the second portion add 5 ml. of 10 per cent potassium iodide solution and titrate with standard thiosulfate solution, using starch as indicator.

HALIDES

Iodide: Many methods have been reported in the literature for the determination of iodide. A good summary of some of the older methods is given by Beckurts[6] and a later critical review of the various methods for the determination of iodide is presented by Leclercq.[7] Only those methods which are of practical importance are discussed below.

(*a*) *Oxidation to Iodate and Titration of Iodate* (Winkler Method): According to Winkler,[8] iodide in weakly acid solution (less than $0.01N$ in acid) is oxidized to iodate with chlorine water. Iodine separates out at first but is oxidized further to iodate by the chlorine:

$$I^- + 3Cl_2 + 3H_2O \longrightarrow IO_3^- + 6Cl^- + 6H^+$$

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[4] F. J. Hallinan and W. R. Thompson, *J. Am. Chem. Soc.*, 61, 265 (1939).

[5] V. L. Spitzer, *Ind. Eng. Chem., Anal. Ed.*, 8, 465 (1936).

[6] H. Beckurts, *Die Methoden der Massanalyse*, Vieweg, Braunschweig, 1913.

[7] L. Leclercq, *J. pharm. Belg.*, 17, 545, 563, 585, 603, 631, 665, 687, 705, 721, 739, 758, 778, 798, 815, 837 (1935); Dissertation, Univ. of Liège, 1935 (Travaux publiés pendant la période 1934–1936, Institut de Pharmacie, A. Gilkinet, Univ. de Liège).

[8] L. W. Winkler, cf. *Z. anal. Chem.*, 39, 85 (1900); *Z. angew. Chem.*, 28, 396 (1914); *Pharm. Zentralhalle*, 63, 386 (1922); 64, 511 (1923).

The excess chlorine is boiled out and the solution is cooled. The iodate in the solution is determined by reducing with iodide in the presence of sulfuric acid:

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

and titrating the iodine liberated with standard thiosulfate solution. By this process, six equivalents of thiosulfate are required for each mole of iodide ion in the sample making the method advantageous for the determination of small amounts of iodide. The procedure yields good results[9] in the absence of large amounts of bromide and iron.

Chlorine water decomposes fairly rapidly and old solutions introduce errors in the procedure. Kolthoff modified the procedure by using freshly prepared solutions of bleaching powder in the presence of succinic acid, instead of chlorine water. Hunter[10] used sodium hypochlorite as oxidant. The excess chlorine or hypochlorite may be removed by boiling the solution for 10 minutes. Alternatively, the excess oxidant may be removed by adding phenol.

The interference of iron can be eliminated by using phosphoric acid instead of sulfuric acid to acidify the iodate-iodide mixture.

Procedure: To 25 ml. of sample solution containing about 60 mg. of iodide add 5 ml. of approximately $4N$ phosphoric acid and then enough freshly prepared 5 per cent bleaching powder solution or chlorine water until the iodine which separates out redissolves and the solution becomes colorless. Add 5 ml. of 10 per cent phenol solution and allow to stand for 5–10 minutes. Add 5 ml. of N potassium iodide solution and titrate with standard $0.1N$ thiosulfate solution, adding starch indicator near the end-point. Each milliliter of $0.1N$ thiosulfate corresponds to 2.115 mg. of iodide.

Notes: (1) Solutions of hypochlorite and of chlorine slowly oxidize to form chlorite. Since chlorite reacts rapidly with iodide but slowly with phenol, freshly prepared solutions of oxidant must be used to avoid error from this cause.

(2) Iron does not interfere in the determination of iodide by this procedure. It may thus be applied to the analysis of iodine-iron syrup. For the determination of iodide in ferrous iodide pills, see Shimizu and Kelley.[11]

(3) Chloride does not interfere but large amounts of bromide do. This interference may be avoided by acidifying with boric acid instead of phosphoric (if chlorine water is used a solution of boric acid and borax is preferable). To the iodide sample solution add 10 ml. of 3 per cent boric acid solution and then hypochlorite. The solution becomes dark brown, gradually lightens as the iodine is oxidized to iodate, and finally becomes pure yellow as bromide is oxidized to

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[9] I. M. Kolthoff, *Z. anal. Chem.*, **60**, 403 (1921).

[10] A. Hunter, *J. Biol. Chem.*, **7**, 336 (1909); cf. E. Kendall, *J. Am. Chem. Soc.*, **34**, 894 (1912).

[11] K. F. Shimizu and E. A. Kelly, *J. Am. Pharm. Assoc., Sci. Ed.*, **31**, 103 (1942); cf. I. M. Kolthoff, *Pharm. Weekblad*, **59**, 1100 (1922).

bromine by the excess hypochlorite. Add 5 ml. of $4N$ phosphoric acid and 5 ml. of 10 per cent phenol solution, shake the solution, add 5 ml. of N potassium iodide solution, and titrate with thiosulfate. Too much time must not elapse between the additions of phenol and of iodide since bromide may reduce some iodate and low results may be found.

(4) Since free iodine is oxidized to iodate, it is determined with iodide by the Winkler method.

(5) The Winkler titration of iodide was used by Straub[12] for the microdetermination of bismuth. The bismuth is precipitated as bismuth oxyiodide by the procedure of Strebinger and Zins.[13] The bismuth oxyiodide is converted to bismuth oxide and iodide with potassium hydroxide and the iodide determined by the Winkler method. The equivalent weight of bismuth in this procedure is 34.83.

Bromine may be used instead of chlorine in the Winkler method to oxidize iodide to iodate.[14] Bromine water is more readily prepared and more stable than chlorine water and is the preferred reagent, especially for microdeterminations of iodide. Sadusk and Ball[15] found that bromine vapor is more suitable than bromine water. They used a slight modification of the procedure of Schockaert and Foster[16] to introduce the vapor. Air (washed with water and dried with calcium chloride) was blown through a gas-washing bottle containing iodine-free bromine (prepared by washing the C.P. product with water)[17] and was delivered just above the surface of the iodide solution in the reaction flask. On swirling the solution, sufficient bromine was dissolved to oxidize the iodide to iodate. Solutions of sodium hypobromite also have been used as oxidant.[18] After the iodide is oxidized to iodate, the excess bromine in the solution is removed by boiling or by adding phenol or aniline, and the iodate is determined iodometrically.

Procedure: Transfer an accurately measured sample containing up to 2 mg. of iodide to a 250 ml. Erlenmeyer flask. Dilute with water to 100 ml. Add methyl orange indicator, neutralize the solution with $2N$ sulfuric acid and add 2 ml. in excess. Add bromine vapor or saturated bromine water until the solution remains yellow. Add a few glass beads and boil the solution on a sand bath until the yellow color disappears and then boil for 2 more minutes. Cool the solution, wash down the sides of the flask with water, add 2 ml. of 10 per cent potassium iodide, swirl the solution gently, and titrate

[12] V. J. Straub, *Z. anal. Chem.*, 76, 108 (1929).

[13] R. Strebinger and W. Zins, *Mikrochemie*, 5, 166 (1927); *Z. anal. Chem.*, 72, 417 (1927); 76, 108 (1929); R. Strebinger and G. Ortner, *ibid.*, 107, 14 (1936).

[14] S. Bugarszky and B. Horvath, *Z. anorg. Chem.*, 63, 184 (1909); cf. T. Leipert, *Mikrochemie Pregl Festschrift*, 1929, 266.

[15] J. F. Sadusk, Jr. and E. G. Ball, *Ind. Eng. Chem., Anal. Ed.*, 5, 386 (1933).

[16] J. A. Schockaert and G. L. Foster, *J. Biol. Chem.*, 95, 89 (1932).

[17] G. M. Karns and H. C. Donaldson, *J. Am. Chem. Soc.*, 54, 442 (1932).

[18] E. Schulek, *Z. anal. Chem.*, 66, 161 (1925); cf. ref. 22.

the liberated iodine with standard thiosulfate solution using starch indicator near the end-point.

Notes: (1) Up to 0.1 mg. of iron does not interfere; if more iron is present, phosphoric acid should be used instead of sulfuric.

(2) Bromide does not interfere unless present in amounts greater than 20 times that of iodide. Chloride may be present in amounts up to 5 g.

(3) Even small amounts (1 mg.) of nitrous acid interfere; however, the interference of as much as 100 mg. of nitrous acid may be eliminated by the azide method of Reith.[19]

(4) Ammonium salts, nitrate, and sulfate may be present in moderate amounts. Large amounts (more than 30 mg.) of mercury salts interfere. Only traces of alcohol may be present; if alcohol is used to extract iodide, it must be evaporated off.

(5) One of the most important applications of the iodometric titration is to the determination of alkoxy groups after decomposing the compound according to the well-known Zeisel procedure. The alkyl iodide so produced is absorbed in bromine water and iodate is formed. The procedure is then similar to that described below. A very full account of the literature on this determination has been given by Elek;[20] this should be consulted for further details.

Kainrath,[21] working with a larger amount of iodide, oxidized the iodide with bromine and obtained good results even if the sample contained 10–100 times as much chloride or bromide as iodide.

Procedure: Transfer the sample solution containing at least 10 mg. of iodide to a 250 ml. Erlenmeyer flask. Dilute to 100 ml. Add 5 ml. of glacial acetic acid, 10–20 ml. of 20 per cent sodium acetate solution and bromine water in excess until the strong iodine color fades. Allow to stand for 10 minutes and add 80 per cent formic acid dropwise, swirling the solution for a few seconds after each addition. After excess bromine is removed, add 5 per cent potassium iodide and dilute sulfuric acid, and titrate the liberated iodine with standard 0.1*N* thiosulfate solution.

For the determination of iodide in a silver halide precipitate, the latter is treated with 5 ml. of glacial acetic acid, 10 ml. of acetate solution, and an excess of bromine water. Heat the mixture on a steam bath for 10 minutes and allow to stand for 30 minutes. Proceed further as described above.

For the determination of iodide in photographic films, proceed as follows. Cut a measured piece of the film into small pieces and place in a dry glass-stoppered flask. Pipette 100 ml. of 5 per cent sodium thiosulfate into the flask and swirl until the silver halides dissolve and the film becomes clear. Filter the solution through a dry filter. To 50 ml. of the filtrate add 15 g. of sodium acetate trihydrate followed by pure bromine from a burette, shaking the solution continuously. After 2 to 3 ml. additions of bromine, the bromine color persists. Allow the solution to stand for 10 minutes. Destroy the excess bromine with formic acid and proceed as described above.

[19] J. F. Reith, *Rec. trav. chim.*, **48**, 386 (1929).

[20] A. Elek, in *Organic Analysis*, Vol. I, Interscience, New York-London, 1953.

[21] P. Kainrath, *Z. anal. Chem.*, **125**, 1 (1942).

Schulek and Endröi[22] use chlorine water in the presence of bromide in alkaline solution to oxidize iodide to iodate.

$$Cl_2 + 2OH^- = ClO^- + Cl^- + H_2O$$
$$ClO^- + Br^- = BrO^- + Cl^-$$
$$I^- + 3BrO^- = IO_3^- + 3Br^-$$

The excess oxidizing agent is then destroyed with cyanide:

$$ClO^- + CN^- + H_2O = ClCN + 2OH^-$$
$$BrO^- + CN^- + H_2O = BrCN + 2OH^-$$

and in alkaline solution:

$$ClCN + 2OH^- = Cl^- + CNO^- + H_2O$$
$$BrCN + 2OH^- = Br^- + CNO^- + H_2O$$

Procedure: Transfer to a 250 ml. glass-stoppered Erlenmeyer flask an accurately measured sample containing 0.2–20 mg. of iodide. Add 10–20 ml. of N sodium hydroxide solution (depending on the bromide content of the sample) and dilute to 30 ml. with water. If the bromide content is too low, add 0.5 g. of potassium bromide. Add 5–10 ml. of freshly saturated chlorine water, shake thoroughly, and allow to stand for 20 minutes. Add 2 ml. of freshly prepared 5 per cent potassium cyanide, shake and add 20 ml. of N sodium hydroxide, and set aside for 10 minutes. Shake the flask and loosen the stopper several times during this period, renewing the liquid round the stopper. Dilute to 100 ml. and add 1 g. of potassium iodide. Acidify with 15 ml. of 10 per cent hydrochloric acid and titrate the liberated iodine with $0.1N$ or $0.01N$ thiosulfate, using starch as indicator. One milliliter of $0.1N$ thiosulfate corresponds to 2.115 mg. of iodide.

Potassium permanganate in alkaline solution has been used to oxidize iodide to iodate.[23] The excess permanganate is reduced with ethanol and the manganese dioxide filtered off. Clark and Jones[24] observed low results by the alkaline permanganate method. They prefer oxidation with permanganate in acid solution and worked out procedures based principally on the work of Groak.[25] The excess permanganate is reduced with potassium nitrite and the nitrous acid removed with sulfamic acid. Large amounts of bromide and chloride do not interfere in this procedure if the liberated elements are boiled out.

For organic compounds, fusion and dry ashing procedures can be eliminated. If the compounds are soluble in acid and not volatilized from boiling solution, they are dissolved in dilute nitric acid and oxidized with permanganate. Nonvolatile compounds, insoluble in acid but soluble in base, are first boiled in alkaline permanganate solution and then acidified to complete the oxidation. Insoluble or volatile organic compounds are first dehalogenated by sodium in absolute ethanol. After dilution with water, the alcohol is removed by boiling and the iodine determined.

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[22] E. Schulek and P. Endröi, *Anal. Chim. Acta*, **5**, 252 (1951).

[23] A. Longi and L. Bonavia, *Gazz. chim. ital.*, **28**, 336 (1898); R. Bernier and G. Peron, *J. pharm. chim.*, (7), **3**, 242 (1911); B. Grützner, *Chem. Ztg.*, **38**, 769 (1914); J. Bucholtz, *Arch. exptl. Path. Pharmacol.*, **81**, 289 (1917); W. F. Baughan and W. W. Skinner, *Ind. Eng. Chem.*, **11**, 563 (1919).

[24] G. R. Clark and J. H. Jones, *J. Assoc. Offic. Agr. Chemists*, **25**, 755 (1942).

[25] B. Groak, *Biochem. Z.*, **175**, 455 (1926).

Procedure: Transfer the sample to a 500 ml. beaker and dissolve in about 100 ml. of water. Add 10–15 ml. of saturated potassium permanganate solution, 10 ml. of concentrated nitric acid, and a few glass beads. Cover with a watch glass and boil gently for 5 minutes. Remove from the heat and wash down the watch glass and sides of beaker with water. (Excess permanganate must be present at this point.) While swirling the contents of the beaker add 10 per cent potassium nitrite solution dropwise until the solution begins to clear. Continue adding potassium nitrite, allowing each drop to react before adding the next, until the solution becomes colorless. Some particles of manganese dioxide should remain. Immediately add 1 per cent potassium permanganate solution in 1 ml. portions until the solution is pink. (If more than 2 ml. is required or if a brown color appears, immediately add 10 ml. of 1 per cent permanganate, heat to boiling, and repeat additions of nitrite and permanganate to a pink color.) Filter the solution rapidly with suction through a medium-porosity, sintered-glass filter into a 500 ml. flask. Rinse the beaker and filter with water. (The filtrate must be pink.) Add potassium nitrite to decolorize the solution until 1 drop excess is added. Add 5 ml. of 10 per cent sulfamic acid solution, wash down the sides of the flask, and swirl the contents until evolution of nitrogen ceases. Cool the solution to room temperature, add 2–3 g. of solid potassium iodide, and titrate the liberated iodine with standard thiosulfate solution using starch as indicator near the end-point. Run a blank titration on the reagents. Each milliliter of $0.1N$ thiosulfate corresponds to 2.115 mg. of iodine.

If large amounts of bromide and chloride are present the procedure is modified slightly. The sample is dissolved in 150 ml. of water, more permanganate solution is added if more than 0.3 g. of chloride or bromide is present, and the boiling is continued until the volume of solution is reduced to 75 or 80 ml.

For the determination of iodine in organic compounds the following modifications are required. (*a*) Nonvolatile, acid-soluble compounds: 15 ml. of saturated permanganate is used and the initial boiling period is extended to 10 minutes. (*b*) Nonvolatile, alkali-soluble, acid-insoluble compounds: dissolve the sample in 2 ml. of 30 per cent sodium hydroxide solution, dilute to 100 ml. with water, add 15 ml. of saturated potassium permanganate and a few glass beads, boil for 5 minutes, remove from the heat, carefully add 10 ml. of concentrated nitric acid, boil for 5 minutes, and complete the analysis as above. (*c*) Insoluble or volatile compounds: place the sample in a 100 ml. round-bottom flask. Add 20 ml. of absolute alcohol, connect a water-cooled condenser to the flask, and add a small piece (0.2–0.5 g.) of metallic sodium through the condenser. After the reaction subsides, heat the solution and reflux rapidly. From time to time add small pieces of metallic sodium until 25–50 times the theoretically required amount is added or until the sodium no longer reacts. Wash down the condenser and transfer the solution to a 500 ml. beaker. Dilute to 200 ml. with water and boil down gently to 100 ml. Continue the analysis as described above.

Willard and Greathouse[26] used excess periodate to oxidize iodide to iodate in neutral to alkaline solution.

$$I^- + 3IO_4^- \longrightarrow 4IO_3^-$$

The excess periodate is then determined iodometrically by the arsenite titration method (cf. p. 273).

(*b*) *Oxidation of Iodide to Iodine:* The distillation method of Volhard is tedious but does give good results.[27] The procedure may be simplified by direct titration of the liberated iodine. Vincent[28] oxidized iodide with iodate and sulfuric acid; the solution was then neutralized with bicarbonate and titrated with thiosulfate. Schirmer[29] neutralized the solution with borax, which is not so basic as bicarbonate. Bromide reacts with iodate in strong acid solutions and thus interferes. Richard[30] improved Vincent's procedure by using tartaric acid, which is then neutralized with disodium hydrogen phosphate. Kolthoff[31] further improved the procedure by allowing the mixture to stand 2–3 minutes before adding phosphate.

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[26] H. H. Willard and L. H. Greathouse, *J. Am. Chem. Soc.*, **60**, 2869 (1938).

[27] E. Müller and G. Wegelin, *Z. anal. Chem.*, **53**, 20 (1914).

Procedure: Transfer 10 ml. of sample solution containing about 100 mg. of potassium iodide to an iodine flask. Add 10 ml. of 0.5 per cent potassium iodate and 10 ml. of 4 per cent tartaric acid. Stopper the flask and allow to stand for 2–3 minutes. Neutralize the acid with 20 ml. of 10 per cent disodium hydrogen phosphate dodecahydrate solution and titrate with thiosulfate solution. Each milliliter of $0.1N$ thiosulfate corresponds to 10.58 mg. of iodine.

Notes: (1) Chloride does not interfere and bromide interferes only when present in large amounts.

(2) The procedure may be used to determine iodide in tincture of iodine. Free iodine is first titrated with thiosulfate and then the total iodide is determined by the above procedure. In this case, however, the solution must be allowed to stand 10 minutes after the addition of tartaric acid and iodate before the excess acid is neutralized.[32] If the iodine separates out in too large crystals, 0.5 g. of potassium iodide should be added after the phosphate in order to dissolve the iodine.

Nitrite oxidizes iodide quantitatively to iodine in acid solution:

$$2NO_2^- + 2I^- + 4H^+ \longrightarrow 2NO + I_2 + 2H_2O$$

After removal of excess nitrous acid and nitric oxide with urea, the liberated iodine may be titrated with thiosulfate. The reaction of iodide with nitrite is rapid, whereas the reaction of urea with nitrite and nitric oxide is slow, so that the urea may be added to the acidified solution before the addition of nitrite.

Procedure:[33] To a 250 ml. iodine flask add 25 ml. of sample solution which is $0.05–0.2M$ in iodide. Add 1 g. of urea, 5 ml. of $0.5M$ sodium nitrite solution, and 5 ml. of $4N$ sulfuric acid. Stopper the flask and allow to stand with frequent shaking for 10 minutes. Cool in an ice bath, add 1–2 g. of potassium iodide to dissolve the liberated iodine, and titrate with standard thiosulfate solution. Shake the contents of the flask well to dissolve iodine in the vapor phase before filtration.

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[28] E. Vincent, *J. pharm. chim.*, (6) **10**, 481 (1899).

[29] W. Schirmer, *Arch. Pharm.*, **250**, 448 (1912); cf. A. Thiel and E. Meyer, *Z. anal. Chem.*, **55**, 177 (1916).

[30] E. Richard, *J. pharm. chim.*, (6) **16**, 207 (1902).

[31] I. M. Kolthoff, *Z. anal. Chem.*, **60**, 403 (1921).

[32] P. Karsten, *Pharm. Weekblad*, **73**, 1658 (1936).

[33] C. A. Abeledo and I. M. Kolthoff, *J. Am. Chem. Soc.*, **53**, 2893 (1931).

Notes: (1) Chloride does not interfere in the procedure, but bromide, if present in more than equivalent amount to iodide, yields high results. It is better to add the sulfuric acid in 1 ml. portions at 5 minute intervals.

(2) Since part of the nitric oxide is present in the gas phase, frequent shaking is necessary to ensure complete reaction with urea. If, at the end of the titration, the color returns quickly, nitric oxide was not removed completely and the determination must be repeated.

(3) Szancer[34] made nitrite and nitric oxide harmless by neutralizing the acid solution with a slight excess of sodium bicarbonate and titrating with arsenious acid.

(4) Very dilute solutions of iodide may be analyzed by this procedure by reducing the amounts of reagents and extracting iodine with chloroform: To 25 ml. of 0.001–0.01N iodide solution, add 0.5 g. of urea, 1 ml. of 0.2M nitrite, 5 ml. of chloroform, and 5 ml. of 4N sulfuric acid. Titrate the iodine (after adding iodide) with thiosulfate after 30 minutes standing. Grange and Fresenius[35] have used a similar procedure for the determination of traces of iodide; however, their method cannot be recommended since nitrite and nitric oxide interfere.

(*c*) *Oxidation of Iodide to Iodine and Titration of Unused Oxidant:* Iodide is oxidized to free iodine by various oxidants. If the liberated iodine is boiled out, the unused oxidant may be determined by back-titration, and the amount of iodide calculated from the amount of oxidant used. In this method, potassium iodate is a convenient reagent.

Procedure:[36] To 10 ml. of sample solution containing about 100 mg. of iodide add 1 g. of benzoic acid and 25 ml. of 0.1N potassium iodate. Boil out the liberated iodine, cool the solution, and add 5 ml. of N potassium iodide and 5 ml. of 4N sulfuric acid. Titrate the liberated iodine with standard thiosulfate solution. Subtraction of the titer from that obtained for a blank yields the titer equivalent to the iodide oxidized.

Notes: (1) Bromide does not interfere if benzoic acid is used; however, it does interfere if sulfuric or succinic acid is used.

(2) Reducing agents in the sample of course interfere.

(*d*) *Oxidation of Iodide to Iodine Cyanide* (Lang Method): In the presence of acid, hydrocyanic acid and an oxidant, such as nitrite, permanganate, bromate, or iodate, iodide is converted quantitatively to iodine cyanide. Since iodine cyanide reacts with thiosulfate according to the reaction

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[34] H. Szancer, *Arch. Pharm.*, 268, 263 (1930).

[35] Grange, *J. prakt. Chem.*, 55, 167 (1852): R. Fresenius, *Anleitung zur quantitativen Analyze*, Vol. II, 1875, p. 482.

[36] I. M. Kolthoff, *Z. anal. Chem.*, 60, 405 (1921).

$$ICN + 2S_2O_3^{2-} + H^+ \longrightarrow I^- + HCN + S_4O_6^{2-}$$

it can be determined by thiosulfate titration after excess oxidant is removed from the solution. Lang[37] used sodium nitrite as oxidant and removed the excess with urea.

Free iodine is converted to iodine cyanide by the procedure. However, free iodine can be titrated directly with thiosulfate so that iodine and iodide can be determined in the presence of one another by carrying out a direct titration and a titration by the method of Lang.

Procedure: Place the sample solution of iodide in a long-necked flask. Add an equal volume (at least 50 ml.) of $2.5N$ hydrochloric or sulfuric acid, 6–8 ml. of $0.5M$ potassium cyanide, starch solution, and 2–3 g. of urea. While swirling the contents of the flask, add $0.5M$ sodium nitrite dropwise until the starch-iodine color disappears. Allow to stand for 10–15 minutes and titrate with $0.1N$ thiosulfate solution.

Notes: (1) Bromide, chloride, and nitrate do not interfere. If bromide is present, the solution becomes reddish-brown near the end of the oxidation because of the formation of iodine monobromide. The latter is transformed to the colorless cyanide when the oxidation is complete.

(2) If iodide and ferrous iron are present together, the following modified procedure gives good results.[38]

Procedure: Place the solution containing about 0.5 millimole of ferrous iodide in a glass-stoppered flask. Add 10 ml. of 25 per cent phosphoric acid and, with thorough shaking, 5 ml. of 10 per cent potassium cyanide solution (if the solution is not shaken vigorously, local excesses of cyanide cause the formation of ferrocyanide and Berlin blue). Dilute the solution to about 100 ml. and titrate with $0.1N$ permanganate to the first appearance of excess permanganate (a = ml. of $0.1N$ permanganate). At this point, iron is oxidized to the trivalent state, and iodide to iodine cyanide. Treat the solution with 5 ml. of N potassium iodide and titrate with standard thiosulfate solution, using starch near the end point (b = ml. of $0.1N$ thiosulfate).

$$\text{Iodide content} = 6.35b \text{ mg.}$$
$$\text{Ferrous content} = 5.58(a - b) \text{ mg.}$$

Phosphoric acid in the solution prevents the oxidation of iodide by ferric iron.

(*e*) *Other Methods:* Willard and Merritt[39] determine iodide by oxidation with ozone to periodate in solutions made alkaline with sodium or potassium hydroxide. (In sodium carbonate solution, the oxidation is mostly to iodate and only partly to periodate.) The periodate is then determined iodometrically (cf. p. 273).

Bromide. (*a*) *Oxidation to Bromate:* Weszelszky[40] devised a method in which bromide is oxidized to bromate by sodium hypochlorite in a bicarbonate medium. The method was examined and improved by van der Meulen.[41] He oxidized in a solution buffered with boric acid and borate and heated to 80–90°.

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[37] R. Lang, *Z. anorg. u. allgem. Chem.*, **122**, 332 (1922).

[38] I. M. Kolthoff, *Pharm. Weekblad*, 62, 913 (1925).

[39] H. H. Willard and L. L. Merritt, Jr., *Ind. Eng. Chem., Anal. Ed.*, 14, 489 (1942).

[40] J. von Weszelszky, *Z. anal. Chem.*, 39, 81 (1900).

$$Br^- + 3OCl^- \longrightarrow BrO_3^- + 3Cl^-$$

The solution must contain a large excess of sodium chloride. At least $2^1/_2$ times the theoretically required amount of hypochlorite must be added; van der Meulen used as reagent a solution about $1N$ in hypochlorite and $0.1N$ in free hydroxide. After the bromide is oxidized to bromate, the excess hypochlorite is destroyed with excess hydrogen peroxide which, in turn, is destroyed by boiling in the presence of osmium tetroxide as catalyst. The bromate is then determined iodometrically by adding iodide and acid, and titrating with thiosulfate.

Szabó[42] independently developed a similar method using potassium bicarbonate as buffer. Various authors have tested the method of van der Meulen and proposed some modifications. D'Ans and Höfer[43] pointed out that the oxidation of bromide to bromate is quantitative only within a definite pH range and suggested the use of sodium dihydrogen phosphate as buffer. Further systematic studies of the method were made by Kolthoff and Yutzy,[44] who also recommended the use of sodium dihydrogen phosphate as buffer. Willard and Heyn[45] showed that the oxidation of bromide to bromate is quantitative only in the range pH 5.5–7.0. They used an acetic acid–acetate buffer to maintain the proper pH. Others have used calcium carbonate[46] and phosphate–sodium hydroxide[47] to adjust the pH.

According to Szabó and Csányi,[48] the oxidation of bromide to bromate by chlorine takes place in two main steps. The first, resulting in the oxidation of bromide to hypobromous acid and/or bromine monochloride, is postulated as involving the following reactions:

$$\begin{aligned} 2Br^- + Cl_2 &\rightleftharpoons Br_2 + 2Cl^- \\ Br_2 + H_2O &\rightleftharpoons BrOH + H^+ + Br^- \\ BrOH + Cl_2 &\longrightarrow BrCl + HOCl \end{aligned}$$

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[41] J. H. van der Meulen, *Chem. Weekblad*, **28**, 82 (1931).

[42] Z. G. Szabó, *Z. anal. Chem.*, **84**, 24 (1931).

[43] J. D'Ans and P. Höfer, *Angew. Chem.*, **47**, 73 (1934).

[44] I. M. Kolthoff and H. Yutzy, *Ind. Eng. Chem., Anal. Ed.*, **9**, 75 (1937).

[45] H. H. Willard and A. H. A. Heyn, *Ind. Eng. Chem., Anal. Ed.*, **15**, 321 (1943)

[46] H. Doering, *Z. anal. Chem.*, **108**, 255 (1937).

[47] J. F. Alicino, A. Crickenberger, and B. Reynolds, *Anal. Chem.*, **21**, 755 (1949).

[48] Z. G. Szabó and L. Csányi, *Anal. Chim. Acta*, **6**, 208 (1952).

The most favorable pH range for this step is said to be between 6.5 and 7.5. The second main step involves the oxidation to bromate which is postulated as involving the following reactions:

$$3BrOH \longrightarrow BrO_3^- + 3H^+ + 2Br^-$$

$$BrCl + 2Cl_2 \longrightarrow BrCl_5$$

$$BrCl_5 + 3H_2O \longrightarrow BrO_3^- + 6H^+ + 5Cl^-$$

This step takes place most readily at a somewhat higher pH than the first step. According to Szabó and Csányi, if bromide is oxidized by chlorine, first at a pH between 6.5 and 7.5 and then at a higher pH, the oxidation to bromate is quantitative without the presence of much chloride as required by the van der Meulen method. On the other hand, if the pH is maintained at the higher value (e.g., 8.5–9.0) from the start, the oxidation of bromide to bromate is quantitative only in the presence of a high chloride concentration.

Other modifications in the van der Meulen method involve the use of sodium formate[49] or phenol[48] to destroy the excess hypochlorite before titrating the bromate, and the use of ammonium molybdate to catalyze the reaction between bromate and iodide before titration with thiosulfate.[44,49] Belcher considers sodium formate preferable to phenol for general purposes.

Procedure of Kolthoff and Yutzy: To 25 ml. (or less) of neutral bromide solution, add 1 g. of sodium dihydrogen phosphate dihydrate, 10 g. of sodium chloride, and 5 ml. of N sodium hypochlorite solution.[50] Heat the solution to boiling and then add 2.5 g. of sodium formate dissolved in 5 ml. of water. Allow to cool, dilute to 150 ml., and add 1.0 g. of potassium iodide, 25 ml. of $6N$ sulfuric acid, and 1 drop of $0.5N$ ammonium molybdate. Titrate the liberated iodine immediately with standard thiosulfate solution using starch near the end-point.

Run a blank titration under identical conditions using a volume of water equal to the volume of sample solution. One milliliter of $0.1N$ thiosulfate solution equals 1.332 mg. of bromide.

Notes: (1) If the sample contains less than 25 micromoles of bromide (2 mg.), the 10 g. of sodium chloride may be omitted in the determination and in the blank.

(2) With 10 ml. or more of $0.01M$ bromide, the error in the method is less than 0.3 per cent; with 10 ml. of $0.001M$ solution, the error is less than 1 per cent.

(3) Organic substances, such as gelatin and dyes, which are brominated easily, must be absent. These substances may be destroyed conveniently as follows.

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[49] J. H. van der Meulen, *Chem. Weekblad*, 28, 238 (1931).

[50] Prepare the solution by the method of van der Meulen: Dissolve 35.5 g. of chlorine in 750 ml. of water containing 44 g. of sodium hydroxide. Dilute to 1 liter. The resulting solution is N in hypochlorite and $0.1N$ in hydroxide; stored in an amber glass bottle in a cool place, the solution is stable for a few days.

Evaporate the sample solution to dryness in a nickel crucible and fuse at a low temperature with sodium peroxide. Take up the residue in hot water and filter. Evaporate the filtrate to a small volume, neutralize to methyl red with hydrochloric acid, and continue with the above procedure.

(4) Chloride does not interfere in the determination of bromide by this method; iodide, however, does interfere. If iodide is present with bromide, the sum of these is determined. Since iodide can be determined in the presence of bromide, the bromide can be determined by difference.

(5) Large amounts of calcium and magnesium cause somewhat low results[51] which are attributed to the difficulty of carrying out an oxidation of bromide to bromate in the presence of a heavy precipitate of calcium and magnesium phosphate.

(6) An application of the modified van der Meulen method to the determination of methyl bromide in air and in products for which it is used as a fumigant is described by Stenger, Shrader, and Beshgetoor.[52]

(7) Some investigators prefer to use commercial sodium hypochlorite solutions suitably diluted to about 5 per cent of sodium hypochlorite.[51,53] This solution has much to commend it on the grounds of convenience, but the bromine-free product should be used.

Procedure of Szabó and Csányi:[48] To the bromide solution containing 0.1–25 mg. of bromide add a mixture of 1 g. of borax and 1 g. of potassium bicarbonate. Add the required amount of chlorine water containing chlorine hydrate.[54] Even for the maximum amount of bromide, 35–40 ml. of chlorine water should suffice. Heat the solution on an asbestos gauze over a gentle flame until vigorous evaporation begins. Continue evaporation until the volume of solution is reduced to 10–20 ml. Remove from the flame, dilute to 50 ml. with distilled water, and remove any remaining chlorine with 5 per cent phenol. Cover the beaker with a watch glass and allow to stand 6 minutes. Dissolve 1 g. of potassium iodide in the solution, acidify with 20 ml. of 20 per cent sulfuric acid, and after 5 minutes titrate the liberated iodine with 0.05N or 0.01N thiosulfate using starch as indicator.

Notes: (1) Substances which are oxidized to a higher oxidation state and consequently react with iodide interfere, e.g., Cr^{3+}, V^{4+}, Fe^{2+}, $Fe(CN)_6^{4-}$, Co^{2+}, Ni^{2+}, As^{3+}, Sb^{3+}, Pb^{2+}, and Mn^{2+}. Copper and iron even in traces decompose hypobromous and hypochlorous acid. Mercury and molybdate are said to decompose catalytically the bromate which is formed by the oxidation.

(2) Low results may be obtained in the presence of substances which consume much chlorine, e.g., sulfite, thiosulfate, sulfide, oxalate, and tartrate.

(3) When interfering substances are present, separation may be necessary. This can be effected by oxidizing the bromide to bromine with permanganate, distilling it over into an alkaline solution, neutralizing the solution with hydrochloric acid, and determining the bromide by the above procedure.

(*b*) *Oxidation to Bromine Cyanide:* Several methods for the determination of bromine have been developed which depend upon the oxidation of bromide to bromine cyanide.

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[51] J. Haslam and G. Moses, *Analyst*, **75**, 343 (1950).

[52] V. A. Stenger, S. A. Shrader, and A. W. Beshgetoor, *Ind. Eng. Chem., Anal. Ed.*, **11**, 121 (1939).

[53] R. Belcher, A. M. G. Macdonald, and A. J. Nutten, *Mikrochim. Acta*, 1954, 104.

[54] Prepare chlorine water by saturating distilled water at 0° with chlorine gas which has been passed through concentrated sulfuric acid and distilled water.

$$Br^- + HCN \longrightarrow BrCN + H^+ + 2e$$

Willard and Fenwick[55] titrated bromide directly in hydrochloric acid solution in the presence of cyanide with permanganate determining the end-point potentiometrically. Lang[56] developed a lengthy procedure using standard potassium iodate as oxidant. Lang also developed an iodometric procedure for the determination of bromide after its oxidation to bromine cyanide. After excess oxidizing agent is removed, the bromine cyanide is decomposed with potassium iodide:

$$BrCN + 2I^- + H^+ \longrightarrow I_2 + Br^- + HCN$$

and the iodine formed is titrated with thiosulfate. This procedure is favored by the slight reactivity of bromine cyanide toward many reducing agents. In acid solution, it is not reduced by arsenite, hydrazine, thiocyanate, oxalate, nitrite, or ferrous ion; it is thus possible to destroy readily the excess oxidant used to oxidize bromide to bromine cyanide without attacking the bromine cyanide.

Procedure: To the bromide solution add 5–10 ml. of syrupy phosphoric acid, 5 ml. of $0.5N$ potassium cyanide, and 10–15 ml. of N potassium permanganate. After 5 minutes, add Mohr's salt carefully until the permanganate color is just discharged. Add 1 g. of potassium iodide and titrate immediately with standard thiosulfate solution using starch as indicator. The equivalent weight of bromide in this procedure is 37.45.

Notes: (1) Chloride does not interfere even when present in large amounts.

(2) Iodide is also determined by this procedure; however, the determination is not accurate because iodide is partially oxidized to higher oxidation states by permanganate. For the determination of iodide and bromide, Lang added 2 drops of $0.01N$ potassium thiocyanate after reduction with ferrous salt, 0.5 g. of potassium bromide, and some starch, and titrated with thiosulfate, adding 1 g. of potassium iodide near the end-point. Both procedures for bromide alone and in the presence of iodide give accurate results.[57]

Berg[58] used bromate to oxidize bromide in the presence of cyanide:

$$BrO_3^- + 2Br^- + 3HCN + 3H^+ \longrightarrow 3BrCN + 3H_2O$$

The excess bromate is then destroyed with bromide and aniline, sulfanilic acid, phenol or *p*-phenolsulfonic acid. The bromine cyanide is titrated iodometrically.

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[55] H. H. Willard and F. Fenwick, *J. Am. Chem. Soc.*, 45, 623 (1923).

[56] R. Lang, *Z. anorg. u. allgem. Chem.*, 144, 75 (1925).

[57] O. Tomíček and A. Jánský, *Collection Czech. Chem. Communs.*, 1, 585 (1929).

[58] R. Berg, *Z. anal. Chem.*, 69, 1 (1926).

Procedure: Dissolve the sample in 50–60 ml. of water. Add 10 ml. of *N* potassium cyanide, enough hydrochloric acid to make its concentration 10 per cent, and 0.1*N* potassium bromate dropwise (1–2 drops per second) until the transitory yellow color of free bromine is no longer evident. At once add 20 ml. of 10 per cent aniline hydrochloride or phenol solution and 10 ml. of 0.1*N* potassium bromide. After 30–60 seconds add 1 g. of potassium iodide and titrate dropwise with standard 0.1*N* thiosulfate solution, using starch as indicator. The equivalent weight of bromide is 24.97 g.

Notes: (1) The procedure yields accurate results only if a slight excess of bromate is used and is destroyed before the chloride can react:

$$BrO_3^- + 2Cl^- + 3HCN + 3H^+ \longrightarrow 2ClCN + BrCN + 3H_2O$$

(2) If iodide is present, it is determined by direct titration with bromate (see p. 526). Bromide is then determined by the above procedure; the bromide formed in the iodide determination is determined together with the bromide present in the sample.

$$BrO_3^- + 3I^- + 3HCN + 3H^+ \longrightarrow 3ICN + Br^- + 3H_2O$$

Schulek[59] oxidized bromide to bromine cyanide with chlorine water in the presence of cyanide. The excess chlorine is bound as chlorine cyanide, which does not react with iodide:[60]

$$Br^- + Cl_2 + CN^- \longrightarrow BrCN + 2Cl^-$$

$$Cl_2 + CN^- \longrightarrow ClCN + Cl^-$$

The bromine cyanide is then reduced by iodide in acid solution, and the liberated iodine titrated with thiosulfate. The procedure is designed for microgram quantities of bromide.

Procedure: Transfer to a 50 ml. glass-stoppered Erlenmeyer flask the sample containing 20–250 μg. of bromide in 8–10 ml. of solution. If necessary, neutralize the solution to methyl red. Add 8–16 drops of fresh saturated chlorine water, shake thoroughly, add 4–8 drops of freshly prepared 5 per cent potassium cyanide solution (use half the number of drops of chlorine water) and shake several times. Loosen the stopper from time to time, renewing the liquid around the stopper. Acidify the solution with 10–15 drops of 10 per cent hydrochloric acid and add 3–4 drops of freshly prepared 20 per cent potassium iodide solution and 2 drops of 1 per cent starch solution. After 10 minutes titrate with standard 0.002*N* sodium thiosulfate solution. Each milliliter of 0.002*N* thiosulfate corresponds to 79.92 μg. of bromide.

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[59] E. Schulek, *Anal. Chim. Acta*, **2**, 74 (1948).

[60] E. Schulek and E. Pungor, *Anal. Chim. Acta* **5**, 137 (1951).

Notes: (1) For smaller amounts of bromide (1.5–20 μg.) smaller amounts of reagents may be used successfully. The volume of sample should be 3–5 ml., and the following amounts of reagents used: 2–3 drops of chlorine water, 1 drop of potassium cyanide solution, 4–5 drops of hydrochloric acid, 2 drops of potassium iodide solution, and 1 drop of starch solution. Titrate with $0.001N$ or $0.005N$ thiosulfate.

(2) For samples containing 1.5–3.5 μg. of bromide, the method yields results which are low by 5–9 per cent; for samples containing 16–240 μg. of bromide, the error is less than ±1 per cent.

(3) The method is unsatisfactory in the presence of iodide, but chloride does not interfere. The procedure can be modified to overcome the interference of iodide, and has been applied to many determinations.[61]

(*c*) *Oxidation to Bromine:* Bugarszky[62] determined bromide in the presence of chloride by oxidizing to bromine in acid solution with iodate, boiling out the free bromine, and determining the excess iodate iodometrically. In the presence of small amounts of chloride, good results are obtained; however, if chloride and bromide are present in equal amounts, chloride begins to interfere. With large amounts of chloride high results are obtained. Iodide is determined with the bromide by this method.

$$2IO_3^- + 10Br^- + 12H^+ \longrightarrow 5Br_2 + I_2 + 6H_2O$$

Several procedures have been described in the literature by which bromide is oxidized to bromine, which in turn is distilled or aerated into a solution of potassium iodide. An equivalent amount of iodine is liberated and titrated in acid solution with standard thiosulfate. Alternatively the bromine may be caught in a standard arsenite solution which is back-titrated with standard iodine.[63]

Clark[64] oxidizes the sample with chromic-sulfuric acid, absorbs the liberated halogens in basic hydrazine solution and determines bromide by Lang's method. Iodide does not interfere since it is oxidized to iodate and not volatilized. Bobtelsky and Rosowskaja-Rossienskaja[65] acidify a chloride solution containing small amounts of bromide with sulfuric acid, and oxidize with potassium dichromate. The liberated bromine is carried over into a potassium iodide solution by a stream of air and titrated with thiosulfate. Under the conditions used, chloride is not appreciably oxidized. For details, the original paper should be consulted.

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[61] E. Schulek, J. Laszlovszky, I. G. Molnar, and E. Zapp, *Z. anal. Chem.*, **134,** 161 (1951).

[62] S. Bugarszky, *Z. anorg. Chem.*, **10,** 387 (1895); cf. L. W. Andrews, *J. Am. Chem. Soc.*, **29,** 275 (1907); I. M. Kolthoff, *Z. anal. Chem.*, **60,** 405 (1921).

[63] H. Baubigny and P. Rivals, *Compt. rend.*, **124,** 859 (1897); P. Clausmann, *Bull. soc. chim., France*, (4) **9,** 188 (1911); W. F. Baughman and W. W. Skinner, *Ind. Eng. Chem.*, **11,** 954 (1919); C. C. Meloche and H. H. Willard, *ibid.*, **14,** 422 (1922); F. W. Edwards, H. R. Nanji, and E. B. Parkes, *Analyst*, **61,** 743 (1936); A. G. Francis and C. O. Harvey, *Biochem. J.*, **27,** 1545 (1933); B. S. Evans, *Analyst*, **56,** 590 (1931).

[64] G. R. Clark, *J. Assoc. Offic. Agr. Chemists*, **28,** 757 (1945).

[65] M. Bobtelsky and R. Rosowskaja-Rossienskaja, *Z. anorg. u. allgem. Chem.*, **199,** 283 (1931).

Bromide may be oxidized to bromine with bromate[66] or with chromic acid;[67] the bromine is extracted in an organic solvent, such as carbon tetrachloride, and titrated iodometrically. The presence of more than 100 mg. of sodium chloride interferes, but iodide is oxidized to iodate and does not interfere.

Chloride: In strong acid solution in the presence of cyanide, chloride is oxidized by bromate according to the reaction

$$2Cl^- + BrO_3^- + 3CN^- + 6H^+ \longrightarrow 2CNCl + BrCN + 3H_2O$$

This is the basis of an iodometric determination of chloride according to Berg[68] (cf. p. 526).

Procedure: Dissolve the sample in 20–30 ml. of water in a glass-stoppered flask. Treat with an accurately measured amount of *ca.* *N* potassium cyanide solution (2–15 ml.) and enough 1:1 sulfuric acid to make its concentration *ca.* 30 per cent. This raises the temperature of the solution to 30–35°. Without cooling, add *N* potassium bromate solution until 8–10 times the theoretically required amount is present. Allow the mixture to stand 45–90 minutes, depending on the chloride content. Alternatively heat the mixture to 35–40°C. for 20–30 minutes to effect quantitative oxidation. Cool the reaction mixture and allow it to flow in a thin stream into a solution containing 50–100 ml. of 10 per cent aniline hydrochloride, about 10 ml. of *N* potassium bromide solution, and 20 ml. of concentrated hydrochloric or 1:1 sulfuric acid. After $^1/_2$ to 1 minute, add enough potassium iodide to make its concentration about 1 per cent and titrate dropwise with standard thiosulfate solution. The equivalent weight of chloride in this determination is 35.44. Run a blank determination on the same amount of potassium cyanide solution because it always contains some chloride.

Notes: (1) At times, especially if large amounts of chloride are present, an iodine addition product of aniline is formed which is distinguishable by the brown-black precipitate. In such cases an excess of thiosulfate may be added and back-titrated with standard iodine solution.

(2) The method yields accurate results even for very small amounts of chloride.

(3) Iodide and bromide are determined with chloride by this procedure (cf. p. 526).

[66] A. Denoël, *J. pharm. Belg.*, 22, 179 (1940).

[67] P. L. Kapur, M. R. Verma, and B. D. Khosla, *Ind. Eng. Chem. Anal. Ed.*, **14**, 157 (1942).

[68] R. Berg. *Z. anal. Chem.*, 69, 1 (1926).

HYPOHALITES

Hypochlorite. (*a*) *Titration in Acid Solution:* In acid solution, hypochlorite oxidizes iodide according to the reaction

$$OCl^- + 2I^- + 2H^+ \rightleftharpoons Cl^- + I_2 + H_2O$$

This reaction was utilized by Bunsen for the determination of available chlorine in bleaching powder and bleach solutions. He added an excess of potassium iodide to the solution of the bleaching materials, acidified with hydrochloric acid, and titrated the liberated iodine.

According to Schultz,[69] chlorate is almost always present in bleach solutions and interferes in the Bunsen procedure if the solution is made too acid; he used acetic acid to acidify the iodide solution of the sample. Treadwell[70] stated that the hydrogen-ion concentration must not exceed $10^{-3}M$ for these determinations. On the contrary, Kolthoff[71] found that the solution may be acidified with sulfuric acid or sparingly with hydrochloric acid without interference from chlorate. He observed that impure solutions of hypochlorite require more thiosulfate when acidified with sulfuric or hydrochloric acid than when acidified with acetic acid. In addition, the starch-iodine color returned after the end-point when acetic acid was used. Kolthoff showed, however, that these phenomena are due to the presence of chlorite in the impure hypochlorite solution rather than to the presence of chlorate. Chlorite is formed when a solution of hypochlorite (or even moist bleaching powder) is allowed to stand. The chlorite, in turn, reacts with iodide in acid solution:

$$ClO_2^- + 4I^- + 4H^+ \longrightarrow Cl^- + 2I_2 + 2H_2O$$

According to Bray,[72] this reaction proceeds indirectly via iodate:

$$3ClO_2^- + 2I^- \longrightarrow 2IO_3^- + 3Cl^-$$

In weakly acid solutions (acetic acid-acetate) the process is slow, whereas in stronger acid solutions (sulfuric or hydrochloric acid) it is practically complete in 2–3 minutes.

With pure hypochlorite solution, the same amount of iodine is liberated with acetic or sulfuric acid. It is possible, therefore, to estimate hypochlorite and chlorite in the presence of one another by proper adjustment of the pH. If the solution containing hypochlorite, chlorite, and excess iodide is titrated immediately after acidification with acetic acid, only hypochlorite is determined. After acidification with sulfuric acid, both hypochlorite and chlorite are determined. In the analysis of bleach mixtures the differentiation between hypochlorite and chlorite is probably unnecessary since chlorite is also a bleaching agent. If they must be differentiated, the above scheme may be used but the arsenite method (p. 264) is more satisfactory.

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[69] Schultz, *Z. angew. Chem.*, 16, 833 (1903).

[70] W. D. Treadwell, *Helv. Chim. Acta*, **4**, 396 (1921).

[71] I. M. Kolthoff, *Rec. trav. chim.*, **41**, 740 (1922).

[72] W. C. Bray, *Z. physik. Chem.*, **54**, 463, 569, 731 (1906); *Z. anorg. u. allgem. Chem.*, **48**, 217 (1906); *J. Phys. Chem.*, **7**, 112 (1903).

Procedure: Weigh accurately about 5 g. of bleaching powder and grind with 5 ml. of water in a porcelain mortar. Transfer the paste quantitatively to a 500 ml. volumetric flask and dilute to the mark with water. Treat a 50 ml. aliquot portion of this solution with 10 ml. of N potassium iodide and 15 ml. of $4N$ sulfuric acid, and titrate with standard $0.1N$ thiosulfate solution. The results are usually expressed in terms of per cent available chlorine.

Notes: (1) If the above procedure is applied to a mixture of halogen compounds, all hypohalites, all halites, bromate, and iodate are determined with the hypochlorite.

(2) Chlorate does not interfere in the determination. If chlorate is to be determined after the hypochlorite determination, the solution must be strongly acidified with hydrochloric acid (cf. p. 271).

(3) If iron is present in the sample, the solution is acidified with phosphoric instead of sulfuric acid in order to prevent the reaction of iron with iodide.

(4) Chloramine T reacts with iodide like hypochlorite:

$$CH_3C_6H_4\text{-}SO_2N(Cl)Na + 2I^- + 2H^+ \longrightarrow CH_3C_6H_4\text{-}SO_2NH_2 + I_2 + Na^+ + Cl^-$$

According to van der Meulen,[73] chloramine T and hypochlorite can be determined in the presence of one another since hypochlorite is destroyed by hydrogen peroxide in alkaline solution whereas chloramine T reacts only very slowly with peroxide at room temperature. The excess peroxide is decomposed with osmic acid as catalyst and the chloramine is determined by the above method. The sum of hypochlorite and chloramine is determined on a separate portion of the sample.

Procedure: To 25 ml. of solution containing less than 5 meq. of hypochlorite and chloramine T, add 5 ml. of N sodium hydroxide solution and 10 ml. of N hydrogen peroxide solution. Shake thoroughly, add 1 ml. of 0.1 per cent osmic acid solution, and again shake thoroughly. After 3 minutes add 10 ml. of N potassium iodide solution and 6 ml. of $4N$ sulfuric acid. Titrate with standard $0.1N$ sodium thiosulfate solution.

(*b*) *Titration with Iodide* (Pontius Method): According to Pontius,[74] a solution of bleaching powder may be titrated in bicarbonate medium with iodide solution until starch, which is added as indicator, is colored pure blue. The reaction involved is:

$$3OCl^- + I^- \longrightarrow IO_3^- + 3Cl^-$$

The reaction mechanism is complex and it is not clear why iodine is formed to color the starch blue at the end-point when a slight excess of iodide is present. In a bicarbonate solution the hydrogen-ion concentration is so small (*ca.* 10^{-8} M) that the reaction

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[73] J. H. van der Meulen, *Chem. Weekblad*, **31**, 558 (1934).

[74] J. Pontius, *Chem. Ztg.*, **28**, 59 (1904).

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

should scarcely go the right.

According to Bray,[75] the reaction of hypochlorite with iodide involves the following steps:

$$HOCl + I^- \longrightarrow OI^- + Cl^- + H^+ \qquad \text{(rapid)} \qquad (1)$$

$$OI^- + I^- + 2H^+ \longrightarrow I_2 + H_2O \qquad \text{(rapid)} \qquad (2)$$

$$3OI^- \longrightarrow IO_3^- + 2I^- \qquad \text{(slow)} \qquad (3)$$

In addition, the free iodine formed in reaction (2) reacts rapidly with hypochlorite to form iodate:

$$5OCl^- + I_2 + H_2O \rightleftharpoons 2IO_3^- + 5Cl^- + 2H^+$$

Kolthoff[76] explains the blue color at the end-point as follows. At the equivalence point of the titration, all the hypochlorite is just consumed and the iodine formed by reaction (2) remains in solution to produce the blue starch–iodine complex. Reaction (2) proceeds sufficiently rapidly in bicarbonate solution to make exact results possible, but it is not instantaneous. Thus, if iodide is added fairly rapidly to a pale blue coloration, the intensity of the color increases on standing. In order to obtain accurate results, the solution must contain a large amount of sodium bicarbonate. If carbonate is also present, the pH of the solution is increased, and iodide is more readily converted to iodate; however, reaction (2) then proceeds so slowly that iodine is not formed until a large excess of iodide is present and the end-point occurs too late. On the other hand, if the solution is weakly acid (e.g., acetic acid-acetate solution), reaction (2) proceeds very rapidly but the decomposition of hypoiodite by reaction (3) is so slow that the end-point appears too early. Only by adding iodide slowly enough to allow reaction (3) to proceed can accurate results be obtained. Under all conditions, it is desirable that the iodide be added slowly for the determination of hypochlorite by the Pontius method.

Procedure: To a 50 ml. aliquot portion of bleaching powder solution (p. 263) add at least 3 g. of sodium bicarbonate and 10 ml. of 0.2 per cent starch. Titrate the solution slowly with standard 0.02*M* potassium iodide solution. At the start of the titration a red-brown color forms where the drops of potassium iodide solution fall; this color disappears on stirring. Toward the end of the titration the color becomes blue-black where the drops of titrant fall, becoming colorless on stirring. Continue the titration slowly until the blue color persists.

Notes: (1) The end-point can be detected more accurately and sharply by using ligroin instead of starch as indicator. The titration is carried out slowly with good shaking after each addition of iodide solution until the nonaqueous layer is permanently violet.

(2) Old hypochlorite solutions do not give a sharp end-point by the Pontius titration because of the interference of chlorite. Chlorite reacts slowly with iodide and the end-point color fades continually until all the chlorite is reacted.

(*c*) *Arsenite Method:* The oxidation of arsenite in alkaline solution by hypochlorite is the basis of a method for determining hypochlorite in the presence of chloride, chlorite, chlorate, and perchlorate.[77]

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[75] W. C. Bray, *Z. physik. Chem.*, **54**, 476 (1906).

[76] I. M. Kolthoff, *Rec. trav. chim.*, **41**, 615 (1922).

[77] F. Foerster and P. Dolch, *Z. Elektrochem.*, **23**, 137 (1917); R. M. Chapin, *J Am. Chem. Soc.*, **56**, 2211 (1934); L. Farkas and M. Lewin, *Anal. Chem.*, **19**, 662 (1947).

With the hypochlorite are determined the other hypohalites, bromite, and iodite.

Procedure: To a 250 ml. Erlenmeyer flask add 25 ml. of standard $0.1N$ arsenite solution and 75 ml. of 5 per cent sodium bicarbonate solution. Mix the solution and add to it a measured amount of sample; the sample size should be selected so that at least 2 ml. of $0.1N$ arsenite remains in excess. After 5 minutes add 2–3 ml. of $2N$ acetic acid dropwise with vigorous stirring until carbon dioxide begins to be evolved. Titrate the excess arsenite with standard $0.05N$ iodine solution, using starch as indicator.

Hypochlorite in Presence of Hypobromite and Hypoiodite: All three hypohalites are determined together by the arsenite method or the iodometric titration in acid solution given above for the determination of hypochlorite. Chapin[78] differentiates hypochlorite from the other hypohalites by utilizing the fact that hypobromite and hypoiodite react rapidly with phenol in alkaline solution whereas hypochlorite reacts very slowly. Thus hypobromite and hypoiodite are removed with phenol and the hypochlorite is determined by the arsenite method.

Procedure: Place the sample in a 250 ml. Erlenmeyer flask and dissolve in 30 ml. of water. Add rapidly a mixture of 10 ml. of 0.5 per cent phenol solution (or more for high hypohalite concentration) and 10 ml. of $2N$ sodium hydroxide with vigorous shaking. The amount of alkali added must be sufficient to make the final alkalinity of the solution at least $0.25N$. Shake for 7–10 seconds and add 25 ml. of standard $0.1N$ sodium arsenite from a 50 ml. beaker. Rinse the beaker twice with distilled water and, 5 minutes later, rinse with 75 ml. of 5 per cent sodium bicarbonate solution. Add $2N$ acetic acid dropwise with vigorous shaking until carbon dioxide begins to be evolved. Titrate the excess arsenite with standard $0.05N$ iodine solution in the presence of starch.

Notes: (1) Hypochlorite, bromite, and iodite are determined by this procedure. Thus this method in conjunction with the arsenite procedure (p. 264) makes possible also the determination of bromite and hypobromite or iodite and hypoiodite in the presence of one another, or the determination of hypohalite in the presence of chlorine, chloride, chlorite, and chlorate, of bromite in the presence of bromine, bromide, hypobromite, and bromate, or of iodite in the presence of iodine and iodate.

(2) If calcium and magnesium are present in the sample, sufficient sodium hydroxide must be added to precipitate these ions and make the final concentration of alkali at least $0.25N$.

(3) A beaker is recommended for the addition of arsenite solution so that the addition may be made as rapidly as possible. In this way, the reaction of phenol can be limited to 7–10 seconds.

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[78] R. M. Chapin, *J. Am. Chem. Soc.*, 56, 2211 (1934); cf. L. Farkas and M. Lewin, *Anal. Chem.*, 19, 662 (1947).

(4) For low concentrations of hypochlorite $0.04N$ arsenite and $0.02N$ iodine solution should be used.

(5) The iodometric titration should be carried out below 20°C. Iodine reacts slowly with phenol but, below 20°, error from this source is negligible.

Hypobromite in Presence of Hypochlorite: Schulek and Endröi[79] developed a method for the determination of hypobromite in the presence of hypochlorite. When hypobromite and hypochlorite are added to a buffered solution containing cyanide, the halogen cyanides are formed.

$$OBr^- + CN^- + H_2O \longrightarrow BrCN + 2OH^-$$

$$OCl^- + CN^- + H_2O \longrightarrow ClCN + 2OH^-$$

In the halogen cyanides, bromine has a positive character whereas chlorine has a negative character; bromine cyanide reacts with iodide whereas chlorine cyanide does not.

$$BrCN + 2I^- + H^+ \longrightarrow I_2 + Br^- + HCN$$

Bromine cyanide can thus be determined iodometrically in the presence of chlorine cyanide.

Procedure: Transfer to a 250 ml. glass-stoppered Erlenmeyer flask the sample containing 0.5–15 mg. of hypobromite-bromine. Depending on the amount of alkali contained by the sample, treat with 100–170 ml. of water, 15–25 ml. of 5 per cent potassium dihydrogen phosphate solution, and 1 ml. of freshly prepared 5 per cent potassium cyanide solution. Quickly and thoroughly shake the solution. Acidify the solution with 25–30 ml. of 10 per cent hydrochloric acid and add 2 g. of potassium iodide. After 30 minutes titrate the liberated iodine with standard $0.01N$ or $0.1N$ thiosulfate solution, using starch as indicator near the end-point. Each milliliter of $0.1N$ thiosulfate solution corresponds to 3.996 mg. of hypobromite-bromine or to 4.796 mg. of hypobromite.

Note: Rupp[80] determined hypobromite and bromate in admixture by first titrating the total amount iodometrically, and then decomposing the hypobromite with hydrogen peroxide and titrating the bromate after removing the excess of hydrogen peroxide.

HALITES

Iodite and Bromite: These halites may exist as intermediate products; they can be determined by the iodometric titration in acid medium or by the arsenite method described for the determination of hypohalites (pp. 264 and 654). Bromite and iodite may be determined by the modified arsenite method (p. 265) in the presence of other halogen compounds except hypochlorite.

Chlorite: Chlorite is determined by the addition of potassium iodide and acid:

$$ClO_2^- + 4I^- + 4H^+ \longrightarrow 2I_2 + Cl^- + 2H_2O$$

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[79] E. Schulek and P. Endröi, *Anal. Chim. Acta*, 5, 245 (1951).

[80] E. Rupp, *Z. anal. Chem.*, 57, 16 (1918).

followed by the titration of the liberated iodine with thiosulfate (cf. p. 262). The method was originally used by Bray,[81] who acidified the solution with dilute sulfuric acid. Jackson and Parsons[82] used acetic acid, whereas Schulek and Endröi[83] used phosphoric acid. Kolthoff[84] reported that the reaction in acetic acid is slow and recommended the use of sulfuric acid or phosphoric acid if iron is present. Brown[85] confirmed the observation of Kolthoff; if sulfuric or phosphoric acid is used, the titration with thiosulfate may be carried out immediately whereas, if acetic acid is used, the mixture must be allowed to stand 5 minutes before titration. The potassium iodide should be added to the chlorite followed by acid; if acid is added first, low results are obtained owing to the formation of chlorine dioxide.

Procedure: To 25 ml. of approximately $0.1N$ chlorite solution in a glass-stoppered Erlenmeyer flask add 15 ml. of 15 per cent potassium iodide solution, 50 ml. of water, and then 15 ml. of 30 per cent acetic acid solution. Stopper, mix, and allow to stand in the dark for 5 minutes. Titrate the liberated iodine with standard $0.1N$ thiosulfate solution.

Note: By this procedure, all hypohalites, all halites, iodate, and part of the bromate are determined if present with chlorite.

Chlorite in Presence of Chloride, Hypochlorite, and Chlorate: Foerster and Dolch[86] determined hypochlorite in the presence of chloride, chlorite, and chlorate by allowing it to react in bicarbonate solution with an excess of standard arsenite solution and then determining the excess arsenite iodometrically (p. 264). After the hypochlorite is removed, potassium iodide is added and the solution is slightly acidified:

$$ClO_2^- + 4I^- + 4H^+ \longrightarrow 2I_2 + Cl^- + 2H_2O$$

The iodine liberated by the chlorite is titrated with thiosulfate.

In order to remove hypochlorite in the presence of chloride, chlorite, and chlorate, Schulek and Endröi[87] utilize the fact that hypochlorite in alkaline solution reacts with cyanide ion to form chlorine cyanide, which does not react with iodide. The chlorite is then determined iodometrically.

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[81] W. C. Bray, *Z. physik. Chem.*, **54**, 576 (1905).
[82] D. T. Jackson and J. L. Parsons, *Ind. Eng. Chem., Anal. Ed.*, **9**, 14 (1937).
[83] E. Schulek and P. Endröi, *Anal. Chim. Acta*, **5**, 368 (1951).
[84] I. M. Kolthoff, *Rec. trav. chim.*, **41**, 740 (1922).
[85] E. G. Brown, *Anal. Chim. Acta*, **7**, 494 (1952).
[86] F. Foerster and P. Dolch, *Z. Elektrochem.*, **23**, 137 (1917).
[87] E. Schulek and P. Endröi, *Anal. Chim. Acta*, **5**, 245 (1951).

Procedure: Transfer to a 250 ml. glass-stoppered Erlenmeyer flask an accurately measured portion of sample containing 0.5–5 mg. of chlorite and any amount of chloride, hypochlorite, and chlorate. Dilute the solution to 70–100 ml. and shake with 2–5 ml. of freshly prepared 5 per cent potassium cyanide solution to remove hypochlorite. Add 0.5–1 g. of potassium iodide and enough 25 per cent phosphoric acid solution to make the concentration of acid 1–1.5 per cent. After 5 minutes titrate the liberated iodine with standard 0.01*N* thiosulfate solution with starch as indicator. Each milliliter of 0.01*N* thiosulfate solution corresponds to 0.0887 mg. of chlorite-chlorine or 0.1687 mg. of chlorite (equivalent weight of chlorite is 16.87).

According to van der Meulen,[88] chlorite and bromate can be determined in the presence of hypochlorite and chloramine T. The latter two compounds are decomposed by hydrogen peroxide at 85–90°C. and the excess hydrogen peroxide also decomposes. The chlorite and bromate in the cooled solution are determined iodometrically.

HALATES

Iodate: Iodate reacts very rapidly with iodide in the presence of acid:

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

Even in weakly acidic solutions the reaction is rapid and quantitative (p. 235).

Several metals, such as barium,[89] lead,[90] thorium,[91] mercury,[92] and bismuth,[93] form slightly soluble iodates (for solubility products, see Table III, Vol. I, pp. 286 ff.). These metals may be precipitated with a slight excess of iodate, and the precipitate may be titrated iodometrically or the excess iodate in the filtrate may be determined. Halides may be determined by treating their solutions with solid silver or mercurous iodate, filtering, and determining the iodate in the filtrate.[94]

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[88] J. H. van der Meulen, *Chem. Weekblad*, **31**, 558 (1934).

[89] K. A. Bogdanov, *Zavodskaya Lab.*, **7**, 793 (1983); F. C. Guthrie, *J. Soc. Chem. Ind.*, **59**, 98 (1940).

[90] C. H. R. Gentry and L. G. Sherrington, *Analyst*, **71**, 31 (1946).

[91] Y. A. Chernikov and T. A. Uspenskaya, *Zavodskaya Lab.*, **9**, 276 (1940); T. Moeller and N. D. Fritz, *Anal. Chem.*, **20**, 1055 (1948).

[92] G. Spacu and P. Spacu, *Z. anal. Chem.*, **96**, 30 (1934); C. H. R. Gentry and L. G. Sherrington, *Analyst*, **70**, 419 (1945).

[93] M. B. Schigol, *Zavodskaya Lab.*, **14**, 276 (1948); R. Castagnou, P. Cazaux, and P. David, *Bull. soc. pharm. bordeaux*, **87**, 20 (1949).

[94] J. Sendroy, Jr., *J. Biol. Chem.*, **120**, 335, 405 (1937); E. J. King and D. S. Bain, *Biochem. J.*, **48**, 51 (1951); K. Avaliani, *Zavodskaya Lab.*, **12**, 179 (1946); *Chem. Abstr.*, **40**, 7071 (1946); R. Belcher and R. Goulden, *Mikrochim. Acta*, **1953**, 290.

Bromate: Bromate reacts with iodide in the presence of mineral acid. The rate of reaction is slower than that of iodate under the same conditions. The kinetics of the reaction of bromate, iodide (or bromide), and acid have been studied by many investigators.[95]

The conclusion appears to be that the rate of the reaction is proportional to the bromate and iodide concentrations, and to the square of the hydrogen-ion concentration. The reaction, therefore, does not proceed directly according to the stoichiometric equation:

$$BrO_3^- + 6I^- + 6H^+ \longrightarrow Br^- + 3I_2 + 3H_2O$$

but requires a first step, such as:

$$BrO_3^- + I^- + 2H^+ \longrightarrow HBrO_2 + HOI$$

which proceeds at a measurable rate followed by instantaneous reaction of hypoiodous and bromous acid with iodide.

Kolthoff[96] studied the reaction of bromate with iodide thoroughly from an analytical viewpoint. Of primary importance is the hydrogen-ion concentration. As the hydrogen-ion concentration is decreased, the rate of reaction of bromate with iodide is decreased. If a bromate solution is treated with iodide in weakly acid solution and titrated immediately with thiosulfate, serious errors result, because free bromic acid remains in the solution and oxidizes part of the thiosulfate to sulfate rather than to tetrathionate:

$$4HBrO_3 + 3H_2S_2O_3 + 3H_2O \longrightarrow 6H_2SO_4 + 4HBr$$

Because of this side reaction too little thiosulfate is required. Errors in excess of 4 per cent were observed; these disappeared when the mixture was allowed to stand for a sufficient period before titration with thiosulfate. Hydrochloric acid is more effective than an equivalent amount of sulfuric acid. For immediate and exact titration with thiosulfate the concentration of hydrochloric or sulfuric acid must be at least $0.5M$. At lower acidity the bromate-iodide reaction goes to completion rapidly if ammonium molybdate is added as catalyst.[97] For example, if 25 ml. of $0.01N$ bromate, 1 ml. of N potassium iodide, 1 ml. of $4N$ hydrochloric acid, and 3 drops of N ammonium molybdate are mixed, the solution may be titrated immediately with thiosulfate. (In the absence of molybdate, the same titration may require as much as 5 per cent less thiosulfate and show a gradual return of the starch-iodine color after the end-point.) If the titration is made only 2 minutes after mixing the reagents, excellent results are obtained (error about 0.2 per cent) even in the titration of $0.001N$ bromate. The addition of molybdate as catalyst is especially valuable in the titration of dilute bromate solution. Titrations are not influenced by light or darkness.

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[95] W. Ostwald, *Z. physik. Chem.*, **2**, 127 (1888); O. Burchard, *ibid.*, p. 796; A. A. Noyes and W. O. Scott, *ibid.*, **18**, 118 (1895); W. Meyerhoffer, *ibid.*, **2**, 585 (1888); G. Magnanini, *Gazz. chim. ital.*, **20**, 377 (1890); W. Judson and J. W. Walker, *J. Chem. Soc.*, **73**, 410 (1898); N. Schilow, *Z. physik. Chem.*, **27**, 513 (1898); **42**, 641 (1903); R. H. Clark, *J. Phys. Chem.*, **10**, 679 (1906).

[96] I. M. Kolthoff, *Z. anal. Chem.*, **60**, 348 (1921).

[97] Cf. W. Ostwald, *Z. physik. Chem.*, **2**, 127 (1888).

Iodate and Bromate in Presence of One Another. The reaction between iodate, iodide, and hydrogen ions is rapid and complete at relatively low hydrogen-ion concentrations, whereas the reaction of bromate with iodide under the same conditions is slow. It is possible, therefore, to titrate iodate in the presence of bromate by controlling the pH and reaction time. After the iodine is titrated with thiosulfate, the solution may be acidified with an excess of strong acid and the iodine liberated by the bromate titrated with thiosulfate. Van der Meulen[98] used aluminium chloride or a mixture of fluoride and hydrochloric acid to control the pH of the solution in the determination of iodate.

Procedure: Transfer to an iodine flask 50 ml. of neutral iodate-bromate solution containing less than 3 meq. of each. Add an excess of potassium iodide (5–10 g.) and 10 ml. of M aluminum chloride solution. Allow the solution to stand 5–10 minutes; titrate the iodine liberated with $0.1N$ thiosulfate. Add 5 ml. of $6N$ hydrochloric acid to the solution and titrate the iodine liberated by the bromate with $0.1N$ thiosulfate.

Note: Instead of aluminum chloride, 1.5 g. of potassium fluoride in 25 ml. of water and 7.5 ml. of N hydrochloric acid may be used. Ten milliliters of N potassium iodide is added and the mixture is titrated with thiosulfate after 2–3 minutes.

Kolthoff and Hume[99] found that the iodate-iodide reaction is rapid and quantitative at pH 4–5, whereas the bromate-iodide reaction is slow enough to be disregarded at pH 5 and somewhat faster at pH 4. By using potassium biphthalate (pH 4) as buffer, they were able to determine iodate in the presence of bromate. Since hydrogen ions are used up in the reaction between iodate and iodide, the pH of the solution is raised slightly so that the rate of reaction between bromate and iodide is negligibly small.

Procedure: Transfer to an iodine flask 25–50 ml. of iodate-bromate solution (containing 2–3 meq. of iodate). Add 2 g. of potassium biphthalate.

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[98] J. H. van der Meulen, *Chem. Weekblad,* **36,** 414 (1939).

[99] I. M. Kolthoff and D. N. Hume, *Ind. Eng. Chem., Anal. Ed.,* **15,** 174 (1943).

Swirl to dissolve, add 3 g. of potassium iodide, and allow to stand 3 minutes. Titrate with 0.1N thiosulfate.

Notes: (1) The approximate ratio of 2 g. of biphthalate to 2.5 meq. of iodate is necessary if results accurate to 0.1 per cent or better are desired. When very large concentrations of bromate are present, the method yields high results. Titration of 0.1N iodate which was 1.8N in bromate gave results about 1 per cent high.

(2) In the titration of 0.01N iodate solutions, the use of 1 g. of potassium biphthalate for 0.1–0.25 meq. of iodate in 10–30 ml. of solution gives satisfactory results.

Schwicker[100] observed that iodate in N hydrochloric acid remains unchanged, whereas bromate is reduced to bromine:

$$2BrO_3^- + 10Cl^- + 12H^+ \longrightarrow Br_2 + 5Cl_2 + 6H_2O$$

After the bromine and chlorine are removed with phenol, the iodate is determined iodometrically.

Procedure: To 50 ml. of iodate-bromate solution add 50 ml. of 2N hydrochloric acid. Allow to stand for 1 hour, then treat with 10 ml. of 5 per cent phenol solution, shake, add potassium iodide, and titrate with thiosulfate.

Chlorate: The reaction of chlorate with iodide and acid is slower than the corresponding reactions of iodate and bromate.

$$ClO_3^- + 6I^- + 6H^+ \longrightarrow 3I_2 + Cl^- + 3H_2O$$

According to Bray,[101] the reaction velocity is proportional to the chlorate ion concentration and the square of the hydrogen-ion concentration, and is a linear function of the concentrations of chloride and iodide ion. This may be explained by the following reactions proceeding simultaneously at a measurable rate:

$$ClO_3^- + I^- + 2H^+ \longrightarrow HClO_2 + HOI$$
$$ClO_3^- + Cl^- + 2H^+ \longrightarrow HClO_2 + HOCl$$

followed by the instantaneous oxidation of hydriodic acid by chlorous, hypochlorous, and hypoiodous acids. The reaction of chlorate with chloride is much slower than its reaction with iodide and can be neglected as a first approximation. The reaction rate constant increases a thousand-fold between 30 and 100 ° C. By the usual logarithmic formula this corresponds to a doubling of the rate of reaction between chlorate and iodide for every 8.6 ° C.

A quantitative iodometric determination of chlorate is possible if a large excess of hydrochloric acid is used. Under these conditions, however, iodide is readily air-oxidized. Molybdate catalyzes the reaction of chlorate with iodide and acid,[102] but unfortunately it also catalyzes the air-oxidation of iodide. Bray[101] observed that ferrous ion catalyzes the reaction of chlorate and iodide. Ferrey found that, if the ferrous sulfate and sulfuric acid concentrations are, respectively, $0.2N$ and $4N$, the reaction is quantitative in 30 minutes even at 13 °C.[103] Hakomori[104] recommends the use of Mohr's salt to catalyze the reaction but since fairly high acidity is required in presence of iron the method is of little practical significance. By the following procedure results accurate to 0.5 per cent can be obtained.

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[100] A. Schwicker, *Z. anal. Chem.*, **110**, 173 (1937).

[101] W. C. Bray, *J. Phys. Chem.*, **7**, 92 (1903).

[102] I. M. Kolthoff, *Z anal. Chem.*, **60**, 352 (1921).

Procedure: To 25 ml. of chlorate solution (*ca.* $0.1N$) add 3 ml. of concentrated hydrochloric acid, then 3 portions of about 200 mg. of sodium bicarbonate to remove air. Add immediately 1 g. of potassium iodide and 22 ml. of concentrated hydrochloric acid. Stopper the flask, shake the contents, and allow to stand for 5 minutes. After this period, titrate the solution with standard $0.1N$ thiosulfate solution.

Note: Williams and Meeker[105] determine micro amounts of chlorate in strong caustic solutions by distilling iodine from the solution after treatment with potassium iodide and acid. The distillate is collected in potassium iodide solution and titrated with standard thiosulfate solution.

A better procedure for the iodometric determination of chlorate was worked out by Ditz[106] and modified by Rupp.[107] Bromide in the presence of about $7.5N$ hydrochloric acid is used to reduce the chlorate. The bromine obtained thereby is determined iodometrically. Kolthoff obtained good results by the following procedure.

Procedure: Place 10 ml. of chlorate solution (*ca.* $0.2N$) in a glass-stoppered Erlenmeyer flask. Add 1 g. of potassium bromide and 20 ml. of concentrated hydrochloric acid (the final acid concentration should be about $8N$). Stopper and shake the flask and allow to stand 5 minutes. Add 100 ml. of 1 per cent potassium iodide solution and titrate the solution with standard $0.1N$ thiosulfate solution.

Notes: (1) Under the above conditions, air-oxidation of iodide does not interfere.

(2) According to Ferrey,[108] quantitative results are obtained if the reaction mixture which is $7.5N$ in hydrochloric acid and contains the theoretical amount of iodide is allowed to stand 5 minutes. If $1\,^1/_2$ times the theoretical amount of iodide is used the reaction is complete within 1 minute.

(3) Atkin[109] used the above procedure for the determination of total halates in sodium hypochlorite after the hypochlorite was titrated with sodium benzene sulfinate. Ackerman,[110] found that sodium benzenesulfinate reacts quantitatively with hypochlorite according to the equation:

$$C_6H_5SO_2Na + NaOCl \longrightarrow C_6H_5SO_3Na + NaCl$$

[103] G. J. W. Ferrey, *Quart. J. Pharm. Pharmacol.*, **5**, 405 (1932).

[104] S. Hakomori, *J. Chem. Soc.* (*Japan*), **43**, 62 (1922).

[105] D. Williams and C. C. Meeker, *Ind. Eng. Chem., Anal. Ed.*, **17**, 535 (1945).

[106] H. Ditz, *Chem. Ztg.*, **25**, 727 (1901).

[107] E. Rupp, *Z. anal. Chem.*, **56**, 580 (1917).

[108] G. J. W. Ferrey, *Quart. J. Pharm. Pharmacol.*, **5**, 409 (1932).

[109] S. Atkin, *Anal. Chem.*, **19**, 816 (1947).

[110] L. Ackerman, *Ind. Eng. Chem., Anal. Ed.*, **18**, 243 (1946).

The end-point is detected with starch-iodide test paper (p. 594). Chlorate does not react with sulfinate. Since chlorate introduces no difficulties in the determination of hypochlorite, it seems simpler to determine the hypochlorite with arsenite solution and after the end-point to determine the chlorate by reduction with the same reagent (cf. pp. 138 and 508).

(4) Ferrous sulfate in hydrochloric acid may be used to reduce chlorate and the ferric ion so formed titrated iodometrically (or the unused ferrous ion titrated oxidimetrically; cf. pp. 80 and 185).

Procedure: To 25 ml. of chlorate solution (*ca.* $0.1N$) add 10 ml. of $4N$ hydrochloric acid and 500 mg. of ferrous sulfate. Boil the solution for 1 minute. Cool to 50°, add 5 ml. of N potassium iodide, and titrate immediately with standard $0.1N$ thiosulfate solution. If the color fades slowly near the end-point, heat the solution to 50° and continue the titration to the end-point.

Periodate. (*a*) *Reduction to Iodate:* In a buffered alkaline solution, periodate is reduced to iodate by iodide:

$$IO_4^- + 2I^- + H_2O \longrightarrow IO_3^- + I_2 + 2OH^-$$

This reaction is the basis of an iodometric method in which the liberated iodine is titrated with standard arsenite.[111] The pH of the solution is best adjusted with a boric acid–borate buffer, although a bicarbonate buffer may also be used.

Procedure: To the periodate solution add 20 ml. of saturated borax solution containing 0.5 g. of boric acid. Then add 2 g. of potassium iodide and titrate the solution with standard $0.1N$ arsenite solution.

Notes: (1) Alternatively, the periodate in a buffered alkaline solution is reduced to iodate with an excess of standard arsenite solution in the presence of iodide as catalyst. The excess arsenite is then titrated with standard iodine solution.[112] In this procedure two standard solutions are required.

Procedure: To 5–25 ml. of periodate solution (neutral to phenolphthalein and containing about 0.5 millimole of periodate) add 5–10 ml. of saturated sodium bicarbonate solution, then 15 ml. of standard $0.1N$ arsenite and 1 ml. of 20 per cent potassium iodide. Allow to stand at room temperature for 15 minutes and titrate the excess arsenite with standard $0.1N$ iodine.

(2) Another procedure for the determination of periodate by reduction to iodate in alkaline solution uses manganous sulfate as reductant.[113] The manganese is oxidized to manganese dioxide, which is separated from the solution and determined iodometrically.

(*b*) *Reduction to Iodine:* In acid solution, periodate is reduced to iodine by iodide:

$$IO_4^- + 7I^- + 8H^+ \longrightarrow 4I_2 + 4H_2O$$

The iodine liberated by the reaction may be titrated with either thiosulfate or arsenite. For each mole of periodate, 8 equivalents of iodine are obtained; this is advantageous in the determination of small amounts of periodate (by reduction to iodate, only 2 equivalents of iodine are liberated). On the other hand, iodate also liberates iodine under the conditions of the determination and is determined with the periodate (cf. p. 273). Each mole of iodate liberates 6 equivalents of iodine.

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[111] E. Müller and G. Wegelin, *Z. anal. Chem.*, **52**, 755 (1913); H. H. Willard and L. H. Greathouse, *J. Am. Chem. Soc.*, **60**, 2869 (1938).

[112] E. Müller and F. Friedberger, *Ber.*, **35**, 2652 (1902); E. Müller and W. Jacob, *Z. anorg. Chem.*, **82**, 308 (1913); P. Fleury and J. Lange, *J. pharm. chim.*, (8) **17**, 107 (1933).

[113] P. Fleury and J. Lange, *J. pharm. chim.*, (8) **17**, 107 (1933).

Several methods have been suggested for the determination of periodate in the presence of iodate using the acid reaction with iodide. Malaprade[114] found that periodate in acid solution is quantitatively reduced by α-glycols to iodate. In a portion of sample, periodate and iodate are determined together by adding iodide and acid and titrating with thiosulfate. To another portion of sample, excess mannitol and acid are added. After about 20 minutes potassium iodide is added and the iodine titrated with thiosulfate as before. The difference in the two titers corresponds to the iodine liberated by periodate.

Schwicker[115] reduced the periodate to iodate in alkaline solution with hydrogen peroxide; the excess hydrogen peroxide was destroyed by boiling. After cooling and addition of iodide and acid, the iodine liberated was titrated with thiosulfate.

Kahane[116] separated periodate from iodate by precipitation with zinc in an ammonia–ammonium chloride medium. The periodate precipitates quantitatively as $Zn_5(IO_6)_2$. After standing for 30 minutes at room temperature, the precipitate is separated and washed with water. It is then dissolved in dilute acid, treated with potassium iodide, and titrated with thiosulfate. The iodate is determined in the filtrate. This procedure seems preferable to the other methods given above.

Periodate forms slightly soluble compounds with various cations. Willard and Thompson[117] determined mercury by precipitation in weakly acidic medium as $Hg_5(IO_6)_2$ followed by iodometric titration of the filtered and washed precipitate. The maximum permissible acidity is $0.15N$ nitric or $0.1N$ sulfuric acid. Mercury in the presence of aluminum, zinc, cadmium, nickel, copper, calcium, and magnesium is determined rapidly, conveniently, and accurately. Iron interferes because it precipitates as ferric periodate. Chloride and other halides prevent the complete precipitation of mercury. If a chloride-containing solution is to be analyzed, mercury may be separated as the metal or as the sulfide, and converted to the nitrate or sulfate, respectively.

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[114] L. Malaprade, *Bull. soc. chim. France*, (4) **43**, 683 (1928); cf. Chapter XI.

[115] A. Schwicker, *Z. anal. Chem.*, **110**, 161 (1937).

[116] E. Kahane, *Bull. soc. chim. France*, **1948**, 70.

[117] H. H. Willard and J. J. Thompson, *Ind. Eng. Chem., Anal. Ed.*, **3**, 398 (1931).

Willard and Boyle[118] quantitatively precipitated potassium as KIO_4 in a solution containing ethanol and ethyl acetate and kept at 0°.

Procedure: Dissolve a chloride-free sample in 4–5 ml. of water. Add 1 g. of periodic acid dissolved in 3 ml. of water. Stir the solution and allow 3–4 minutes for potassium periodate to precipitate. Add 90 ml. of solvent containing equal volumes of aldehyde-free ethanol and anhydrous ethyl acetate. Allow the mixture to stand in an ice bath for 30 minutes with continuous mechanical stirring. Filter the solution through a Gooch (or sintered-glass) crucible and wash the precipitate with anhydrous ethyl acetate cooled to 0 °. Place the crucible in a 250 ml. beaker and add 125 ml. of solution containing 5 g. of boric acid and 5 g. of borax. After the precipitate dissolves, add 3 g. of potassium iodide and titrate the liberated iodine with $0.1N$ arsenite solution. The latter solution is best standardized against pure potassium periodate.

Notes: (1) Chloride (and other halides) interfere by reducing periodic acid. They are removed readily by evaporating to dryness a solution of the sample in 10 ml. of concentrated nitric acid. Moderate amounts of sulfate do not interfere; neither do free nitric, phosphoric, sulfuric, and boric acids. In the presence of perchlorate, the results are slightly low.

(2) As much as 100 mg. of sodium does not interfere. Moderate amounts of magnesium, calcium, lithium, aluminum, zinc, nickel, and cobalt do not interfere, but ammonium, iron, manganese, and chromium do interfere. Rubidium and cesium behave like potassium. When calcium and sulfate are present together, low results are obtained, possibly because of precipitation of the double salt $CaSO_4 \cdot K_2SO_4$.

Rogers and Caley[119] devised an empirical method for the determination of lithium by precipitation as a complex periodate with potassium periodate and potassium hydroxide. The composition of the precipitate depends on the method of precipitation and washing, but is constant under fixed conditions. If the same procedure is always used, fairly accurate results for lithium may be obtained by titrating the periodate in the precipitate iodometrically.

Willard and Thompson[120] separated lead from nickel, copper, zinc, cadmium, aluminum, calcium, and magnesium by precipitation as $Pb_3H_4(IO_6)_2$ with sodium periodate in $0.025N$ nitric acid. The periodate in the precipitate was determined by the Andrews method (p. 457) after dissolution in excess standard arsenite, but can be determined iodometrically.

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[118] H. H. Willard and A. J. Boyle, *Ind. Eng. Chem., Anal. Ed.*, 13, 137 (1941).

[119] L. B. Rogers and E. R. Caley, *Ind. Eng. Chem., Anal. Ed.*, 15, 209 (1943).

[120] H. H. Willard and J. J. Thompson, *J. Am. Chem. Soc.*, 56, 1828 (1934); *Ind Eng. Chem., Anal. Ed.*, 6, 425 (1934).

2. Acids. Acids may be determined iodometrically by utilizing the reaction

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

The acid solution is treated with an excess of neutral iodide and iodate, and the liberated iodine titrated with standard thiosulfate. The reaction is practically instantaneous in solutions of high hydrogen-ion concentration and becomes slower as the hydrogen-ion concentration decreases. The reaction velocity is increased appreciably with increased temperature, but iodine becomes more volatile so that pressure bottles must be used.

Kjeldahl[121] used this method in his well-known method for the determination of nitrogen in organic compounds. Gröger[122] pointed out that large amounts of the very weak carbonic acid interfere by reacting to a slight extent with the iodate-iodide mixture. He found that the moderately stronger acids, such as oxalic, tartaric, and acetic, also react incompletely even after 24 hours.

Kolthoff[123] confirmed the fact that the method yields excellent results with strong acids. Even with dilute solutions (e.g., $10^{-3}N$) accurate results are obtained if the iodate-iodide reaction mixture is allowed to stand for at least 15 minutes before titration. Weak acids cannot be titrated directly by this method because the pH at the end-point is too high to effect complete reaction. For example, 25 ml. of $0.1N$ tartaric acid treated with 5 ml. of N potassium iodide and 5 ml. of 3 per cent potassium iodate, when titrated immediately, requires only 23.2 ml. of $0.1N$ thiosulfate; after 20 minutes standing 24.20 ml. is required; by heating the solution for 10 minutes in a pressure bottle the theoretical amount of thiosulfate is required. Malic acid behaves like tartaric acid but citric, succinic, acetic, and benzoic acids cannot be determined. Formic, lactic, and salicylic acids react almost completely in 30 minutes. Bruhns[124] observed that oxalic acid may be titrated iodometrically in the presence of calcium or magnesium salts; oxalate ion is precipitated by these cations, setting free the hydrogen ion as a strong acid. Kolthoff found that the anions of organic hydroxy acids form complex compounds with calcium, barium, magnesium, and zinc and thereby behave as strong acids in the iodometric determination. Tartaric, citric, lactic, and malic acids may be determined quantitatively by adding to 25 ml. of *ca.* 0.1*N* acid, 5 ml. of *N* potassium iodide, 5 ml. of 3 per cent potassium iodate, and 4 g. of calcium or magnesium chloride or 3 g. of barium chloride or zinc sulfate and titrating after 30 minutes with standard thiosulfate. This method is not applicable to organic acids, such as acetic, benzoic, and succinic acids, which contain no hydroxyl group and are consequently only slightly affected by the alkaline earth metal ions. Phosphoric acid cannot be determined accurately by the normal procedure, but in the presence of zinc and ammonium ions a precipitate of zinc ammonium phosphate forms so that the acid behaves as a tribasic acid; in the presence of calcium and magnesium salts, phosphoric acid behaves like an acid having from 2 to 3 ionizable hydrogen ions.

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[121] J. Kjeldahl, *Z. anal. Chem*, **22**, 366 (1883); *cf.* E. Pflüger and K. Bohland, *ibid.*, **24**, 635 (1885).

[122] M. Gröger, *Z. angew. Chem.*, **3**, 353 (1890).

[123] I. M. Kolthoff, *Pharm. Weekblad*, **57**, 63 (1920).

[124] G. Bruhns, *Z. anal. Chem.*, **55**, 45 (1916).

In titrating weak acids, Kolthoff[125] found that the addition of thiosulfate in excess to the solution of acid containing iodide and iodate, followed by the titration of the excess thiosulfate with iodine after a sufficient time interval, resulted in a more quantitative determination of the acid. In the presence of thiosulfate, the iodine concentration remains so small that the reaction

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$$

proceeds quite rapidly even if the hydrogen-ion concentration is very small. Carboxylic acids, such as acetic, succinic, benzoic, oxalic, tartaric, and citric acids, may be determined quantitatively by treating 20 ml. of *ca.* 0.1*N* solution of the acid with 1 g. of potassium iodide, 5 ml. of 3 per cent potassium iodate, and 25 ml. of standard 0.1*N* thiosulfate solution, and back-titrating with standard iodine solution after 15–30 minutes standing. The pH at the end-point is about 7.0–7.3. Acids having dissociation constants of 10^{-6} may be determined in this way. If the reaction mixture is allowed to stand for 20 hours before back-titration with iodine, the pH at the end point is about 8.0. If the solution is 10 times as dilute (i.e., 20 ml. of *ca.* 0.01*N* acid solution, 100 mg. of potassium iodide, 5 ml. of 0.3 per cent potassium iodate, and 25 ml. of 0.01*N* thiosulfate) and the back-titration with iodine is made after 5 minutes, the pH is 6.3; after 10 minutes, 6.4; and after 90 minutes, 6.7.

Thiosulfate is not decomposed by acid if the iodide and iodate are added to the acid before the thiosulfate. The reaction of iodide with iodate in acid solution is very rapid, so that the hydrogen-ion concentration is made small enough to eliminate the side reaction. On the other hand, it is not permissible to accelerate the iodide-iodate reaction for the determination of weak acids by heating since thiosulfate may then react with hydrogen ions.

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[125] I. M. Kolthoff, *Chem. Weekblad*, **23**, 260 (1926).

The iodometric procedure for the determination of weak acids was modified by Kamath and Mainkar[126] for the determination of carboxylic acids in lac. Since lac is insoluble in water and soluble in alcohol, difficulties were encountered in the sensitivity of the starch end-point. By a proper choice of solvents and the use of excess potassium iodide, Kamath and Mainkar obtained excellent results which were superior to those obtained by an alkalimetric titration since lac resin is saponified readily by alkali.

Evans[127] used the iodometric determination of acid for the determination of beryllium. The original paper should be consulted for details.

3. Alkali. Iodine reacts with alkali to form hypoiodite and iodide. The hypoiodite then disproportionates, especially with heat, to form iodate and iodide.

$$\begin{aligned} 2NaOH + I_2 &\longrightarrow NaOI + NaI + H_2O \\ 3NaOI &\longrightarrow NaIO_3 + 2NaI \end{aligned}$$

When the alkali completely reacts with iodine, the overall reaction is

$$6NaOH + 3I_2 \longrightarrow NaIO_3 + 5NaI + 3H_2O$$

An iodometric method for the determination of alkali is based on this reaction.[128] After the excess iodine is removed, the iodate formed by the alkali is titrated with thiosulfate after the addition of iodide and acid.

4. Oxygen and Oxygen Compounds. *Oxygen* (Winkler Method): The classical method of Winkler[129] is the best chemical method for the determination of oxygen dissolved in water. In this sensitive method, manganous hydroxide in alkaline solution is quickly oxidized by dissolved oxygen. The oxidized manganous hydroxide on acidification in the presence of iodide liberates an amount of iodine equivalent to the dissolved oxygen initially present; this is determined readily by titration with thiosulfate.

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[126] N. R. Kamath and V. B. Mainkar, *Anal. Chem.*, 22, 724 (1950).

[127] B. S. Evans, *Analyst*, 60, 291 (1935).

[128] G. S. Smith, *Analyst*, 62, 590 (1937).

[129] L. W. Winkler, *Ber.*, 21, 2843 (1888); 22, 1764 (1889); *Z. anal. Chem.*, 53, 665 (1914); *Z. Untersuch. Nahr. u. Genussm.*, 29, 121 (1915); *Z. angew. Chem.*, 29, 44 (1916); *Die chemische Analyse: Ausgewählte Untersuchungsverfahren fur das chemische Laboratorium*, Enke, Stuttgart, 1931, p. 55; cf. E. J. Theriault, *The Determination of Dissolved Oxygen by the Winkler Method*, Public Health Bulletin No. 151, Govt. Printing Office, Washington, D.C., 1925; *Standard Methods for the Examination of Water and Sewage*, 9th ed., American Public Health Association, New York, 1946, p. 124.

Pomeroy and Kirschman[130] recommend a modification of the procedure generally followed by replacing the alkaline-iodide solution which is $12.5N$ in alkali and $0.9N$ in iodide, with one which is $10N$ in sodium hydroxide and $6N$ in sodium iodide. The marked increase in iodide concentration results in reduced interference by reducing agents, such as organic matter often present in polluted waters or oxalate added in pretreatment procedures. The high concentration of iodide is also beneficial in decreasing the loss of iodine vapor and in sharpening the end-point of the titration.

Reagents: (1) Manganous Sulfate Solution. Dissolve 480 g. of $MnSO_4, 4H_2O$ (or 400 g. of $MnSO_4, 2H_2O$) in distilled water and dilute to 1 liter. The solution when added to an acidified solution of potassium iodide should not liberate more than traces of iodine.

(2) Alkaline Iodide Solution. Dissolve 400 g. of sodium hydroxide and 900 g. of sodium iodide in distilled water and dilute to 1 liter. The solution should be nitrite-free and practically free of carbonate; when diluted and acidified, it should give no color with starch.

Procedure: The determination is carried out in a 250 ml. heavy-walled, glass-stoppered bottle whose volume is accurately known. Fill the bottle with the test solution. If the solution is saturated with air, it may be simply poured into the bottle; otherwise, the sample should be transferred to the bottle in such a way as to ensure at least a three-fold displacement of liquid in the bottle without entrainment of air bubbles or exposure to air. Add 1 ml. of the manganous sulfate solution followed by 1 ml. of alkaline iodide solution, both added well below the surface of the liquid; this may be accomplished with 1 ml. pipettes or burettes having long delivery tips sealed on. Stopper the bottle and mix the contents well by inverting and shaking several times. The dissolved oxygen reacts completely within about 1 minute. Allow the precipitate to settle and add 2 ml. of 1:1 sulfuric acid solution. Stopper the bottle and shake the contents thoroughly. The precipitate dissolves quickly and liberates iodine equivalent to the original dissolved oxygen. Titrate an aliquot portion of the solution with standard $0.01N$ thiosulfate solution. In calculating the dissolved oxygen content, it is necessary to take into account the volume of sample displaced by the reagents (2 ml.). The equivalent weight of oxygen is 8.00.

Notes: (1) Readily oxidizable substances, such as ferrous and nitrite salts, interfere. If the sample contains more than about 10 parts per million of ferric ion, 4 ml. of 85 per cent phosphoric acid should be used instead of sulfuric acid to acidify the solution.

(2) The nitrite interference may be eliminated by the sodium azide modification

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[130] R. Pomeroy and H. D. Kirschman, *Ind. Eng. Chem., Anal. Ed.*, **17**, 715 (1945).

of the Winkler method.[131] Azide reacts quickly with nitrite to form nitrogen, and may be used to pretreat the acidified sample or may be added with the alkaline iodide solution. If a water sample cannot be analyzed immediately, Placak and Ruchhoft[131] recommend a preliminary treatment with 0.7 ml. of concentrated sulfuric acid and 0.8 ml. of 2 per cent sodium azide to prevent reaction of dissolved oxygen. To complete the determination add 1 ml. of manganous sulfate solution, and 3 ml. of alkaline iodide solution and follow the Winkler procedure.

Winkler overcame the interference of nitrite by adding 0.5 g. of sodium hydroxide instead of the 1 ml. of alkaline iodide solution and acidified later with 5 ml. of 50 per cent sulfuric acid. The nitrite is oxidized to nitrate by the manganite in 1–2 minutes; then potassium iodide is added and the liberated iodine titrated with thiosulfate. The nitrite content of the water is determined by adding to another portion of sample 10 ml. of $0.01N$ permanganate and 5 ml. of 50 per cent sulfuric acid; after several minutes, the excess permanganate is back-titrated.

(3) If the sample contains appreciable amounts of ferrous and nitrite salts, the Winkler method may be modified with a permanganate pretreatment to oxidize these interfering substances.[132] If the sample contains large amounts of organic matter, such as sugars, starches, and sewage, this modification may prove detrimental.

(4) For the determination of oxygen in sulfite wastes from paper mills which may contain sulfites, thiosulfates, polythionates, free chlorine, or hypochlorite, the Winkler method is modified to include a pretreatment of the sample with alkaline hypochlorite followed by the addition of acid and iodide, and titration of the liberated iodine with sulfite.[133]

(5) Water samples containing suspended mud and sludge which interfere in the Winkler method may be analyzed for dissolved oxygen if the suspended solids are removed by alum flocculation.[134]

(6) For the determination of dissolved oxygen in small samples by the Winkler method, Krogh[135] used a 10 ml. syringe as the reaction vessel and obtained good results.

(7) The Winkler method was used by Winslow and Liebhafsky[136] for the determination of traces of oxygen (0.0001–0.1 per cent by volume) in inert gases. A special 1 liter sampling and reaction vessel was used.

(8) The variables in the Winkler method for determining 0–4 per cent oxygen by volume in hydrocarbon gases were studied by Taylor and Alexander and by van Straten.[137] They found that the manganous chloride concentration and the

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[131] G. Alsterberg, *Biochem. Z.*, **159**, 36 (1925); cf. C. C. Ruchhoft, W. A. Moore, and O. R. Placak, *Ind. Eng. Chem., Anal. Ed.*, **10**, 701 (1938); O. R. Placak and C. C. Ruchhoft, *ibid.*, **13**, 12 (1941); G. R. Barnett and E. Hurwitz, *Sewage Works J.*, **11**, 781 (1939); *Standard Methods for the Examination of Water and Sewage*, 9th ed., American Public Health Association, New York, 1946, p. 129.

[132] S. Rideal and G. G. Stewart, *Analyst*, **26**, 141 (1901); cf. C. C. Ruchhoft, W. A. Moore, and O. R. Placak, *Ind. Eng. Chem., Anal. Ed.*, **10**, 701 (1938); O. R. Placak and C. C. Ruchhoft, *ibid.*, **13**, 12 (1941).

[133] E. J. Theriault and P. D. McNamee, *Ind. Eng. Chem., Anal. Ed.*, **4**, 59 (1932).

[134] C. C. Ruchhoft and W. A. Moore, *Ind. Eng. Chem., Anal. Ed.*, **12**, 711 (1940).

[135] A. Krogh, *Ind. Eng. Chem., Anal. Ed.*, **7**, 131 (1935).

[136] E. H. Winslow and H. A. Liebhafsky, *Ind. Eng. Chem., Anal. Ed.*, **18**, 565 (1946); cf. L. P. Pepkowitz and E. L. Shirley, *Anal. Chem.*, **25**, 1718 (1953).

[137] G. W. Taylor and D. S. Alexander, *Anal. Chem.*, **24**, 1083 (1952); H. A. C. van Straten, *Anal. Chim. Acta*, **10**, 243 (1954); cf. American Society for Testing Materials Method D1021-53T.

reaction time are very important for accurate results. The manganous chloride concentration is made low so as to give a finely divided precipitate of manganous hydroxide. Hydrogen sulfide and cyanide are removed by scrubbing the gas with caustic solution. Saturated and unsaturated hydrocarbons, including acetylene, carbon dioxide, and carbon monoxide, do not interfere.

Ozone: Ozone oxidizes iodide according to the equation

$$O_3 + 2I^- + H_2O \longrightarrow O_2 + 2OH^- + I_2$$

The gas is absorbed in an iodide solution and after acidification the liberated iodine is titrated with thiosulfate.

Lechner[138] reported that the absorption solution must be alkaline to prevent loss of iodine vapor, but Riesenfeld and coworkers[139] found serious errors in alkaline solutions due to the reaction

$$I^- + O_3 \longrightarrow IO_3^-$$

and recommended the use of boric acid in the absorption solution to neutralize the hydroxide formed in the ozone-iodide reaction. Strongly acid absorption solutions, on the other hand, yield high results[140] due to the reaction

$$4O_3 + 10I^- + 10H^+ \longrightarrow H_2O_2 + 5I_2 + 3O_2 + 4H_2O$$

Procedure: Place 100 ml. of 2 per cent potassium iodide solution in a gas absorption vessel and pass the gas sample through the solution. Add 10 ml. of *M* sulfuric acid and titrate with standard thiosulfate solution.

Note: Ruyssen[140] obtained high results also in boric acid-buffered absorption solution but obtained good results in buffers with pH between 7 and 9.2. Boelter and coworkers,[141] on the other hand, observed that boric acid and pH have no effect on the accuracy of the determination in the pH range 2.3–12.3. Birdsall *et al.*,[142] in agreement with Ruyssen, obtained high results when the ozone was absorbed in boric acid-saturated iodide solution. They explain the discrepancy with the results of Boelter *et al.* by the fact that these authors absorbed ozone in iodide solution without much agitation, so that the hydroxide formed by the reaction of ozone with iodide raised the pH at the reaction surface over that in the bulk of the solution. They suggest that, if the ozone is absorbed with vigorous agitation, the acid error is obtained in solutions buffered at pH 4.6.

After absorption of the ozone, the solution must be acidified with strong acid before titration with thiosulfate. If this is not done, large errors result from a failure of iodate formed in the absorption process to react with thiosulfate. The iodate is probably formed by the reaction

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[138] G. Lechner, *Z. Elektrochem.*, **17,** 412 (1911).

[139] E. H. Riesenfeld and F. Bencker, *Z. anorg. u. allgem. Chem.*, **98,** 167 (1916); E. H. Riesenfeld and G. M. Schwab, *Ber.*, **55,** 2088 (1922); E. H. Riesenfeld, *Angew. Chem.*, **45,** 309 (1932).

[140] B. C. Brodie, *Phil. Trans.* **162,** 435 (1874); F. P. Treadwell and E. Anneler, *Z. anorg. Chem.*, **48,** 86 (1905); R. Ruyssen, *Natuurw. Tijdschr.*, **14,** 245 (1932); **15,** 125 (1933).

[141] E. D. Boelter, G. L. Putnam, and E. I. Lash, *Anal. Chem.*, **22,** 1533 (1950).

[142] C. M. Birdsall, A. C. Jenkins, and E. Spadinger, *Anal. Chem.*, **24,** 662 (1952).

$$3I_2 + 6OH^- \rightleftharpoons IO_3^- + 5I^- + 3H_2O$$

Hydrogen Peroxide: Hydrogen peroxide reacts with iodide in acid solution according to the equation

$$H_2O_2 + 2I^- + 2H^+ \longrightarrow I_2 + 2H_2O$$

According to Noyes and Scott,[143] the rate of formation of iodine may be expressed by the equation

$$\frac{d[I_2]}{dt} = k_1{}^0[H_2O_2][I^-] + k_1[H_2O_2][I^-][H^+]$$

Bray[144] interpreted this rate by postulating the occurrence of two independent rate-determining reactions:

$$H_2O_2 + I^- \xrightarrow{k_1{}^0} H_2O + IO^-$$

$$H_2O_2 + I^- + H^+ \xrightarrow{k_1} H_2O + HOI$$

followed by a rapid reaction of the hypoiodite and hypoiodous acid with iodide:

$$HOI + I^- + H^+ \longrightarrow I_2 + H_2O$$

Liebhafsky and Mohammed[145] carefully reexamined the kinetics of the reaction and confirmed the results above. They calculated for the velocity constants at 25° C. the values $k_1{}^0 = 0.69$ and $k_1 = 10.5$. Thus the reaction is accelerated by hydrogen ions. The effect of temperature on these constants is expressed by the equations

$$k_1{}^0 = 4.91 \times 10^9 e^{-13,400/RT} \text{ from 0 to 50° C.}$$
$$k_1 = 4.58 \times 10^8 e^{-10,450/RT} \text{ from 0 to 40° C.}$$

The reaction of hydrogen peroxide with iodide proceeds at a measurable rate and there is no complete agreement in the literature regarding the applicability of the reaction to the determination of hydrogen peroxide.[146]

The effect of catalysts on the velocity of the peroxide-iodide reaction has been studied by many workers.[147] Of analytical importance is the catalytic activity of molybdic and tungstic acids reported by Brode.[148] Kolthoff[149] utilized the catalytic action of molybdate in the iodometric determination of peroxide, which is especially valuable in the analysis of dilute peroxide solutions and in the determination of peroxide in the presence of substances which slowly react with the liberated iodine, e.g., the determination of hydrogen peroxide in the presence of amyl alcohol.[150]

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[143] A. A. Noyes and W. O. Scott, *Z. physik. Chem.*, **18**, 118 (1895); A. A. Noyes, *ibid.*, **19**, 599 (1896).

[144] W. C. Bray, *Z. physik. Chem.*, **54**, 463 (1906).

[145] H. A. Liebhafsky and A. Mohammed, *J. Am. Chem. Soc.*, 55, 3977 (1933).

[146] E. Lenssen, *J. prakt. Chem.*, **81**, 279 (1860); **82**, 50, 293 (1861); **85**, 89 (1862); C. T. Kingzett, *Chem. News*, **41**, 76 (1880), *J. Chem. Soc.*, **37**, 802 (1880); E. Schöne, *Z. anal. Chem.*, **18**, 133 (1879); H. Thoms, *Arch. Pharm.*, **225**, 335 (1887); **238**, 301 (1900); E. Rupp, *ibid.*, **238**, 156 (1900).

[147] W. Manchot and O. Wilhelms, *Ber.*, **34**, 2479 (1901); *Ann.*, **325**, 93, 105 (1902); M. Traube, *Ber.*, **17**, 1062 (1884); W. Manchot and F. Glaser, *Z. anorg. u. allgem. Chem.*, **27**, 420 (1901).

Procedure: To a measured 25 ml. portion of *ca.* $0.1N$ peroxide solution add 10 ml. of $4N$ sulfuric acid, 6 ml. of N potassium iodide, and 3 drops of N ammonium molybdate. Titrate the solution with standard thiosulfate solution.

Note: If molybdate is not used, the reaction mixture must be allowed to stand in a closed vessel for 15 minutes before it is titrated with thiosulfate.

Rupp and Mielck[151] determined hydrogen peroxide by another procedure. Iodine oxidizes the peroxide in alkaline solution according to the equation

$$H_2O_2 + OI^- \longrightarrow H_2O + O_2 + I^-$$

Procedure: To 25 ml. of dilute peroxide solution in a glass-stoppered flask add 10 ml. of approximately N sodium hydroxide followed by an excess of standard $0.1N$ iodine solution (the order must not be reversed). After 5 minutes, acidify the solution with dilute hydrochloric or sulfuric acid and titrate with standard thiosulfate.

Notes: (1) The method was used successfully with hydrogen peroxide, sodium peroxyborate, and potassium peroxycarbonate. Peroxysulfates do not react with hypoiodite at room temperature.

(2) To obtain better results, boil out the oxygen from the solution before it is acidified.

(3) Since the direct titration in acid is excellent, this procedure is of little practical importance.

Inorganic Peroxides: The soluble peroxides, such as the alkali metal, alkaline earth metal, zinc, cadmium, and mercury peroxides, may be determined in acid solution exactly like hydrogen peroxide. Peroxycarbonates and peroxyborates may also be determined.

Some of the soluble peroxides, such as sodium peroxide, may evolve oxygen when the solid is dissolved in water, and are consequently not determined quantitatively. The solid peroxides are best dissolved by adding slowly with vigorous stirring to an excess of dilute sulfuric acid. Mattner and Mattner[152] found the following procedure to give the best results in the analysis of sodium peroxide and other peroxides.

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[148] J. Brode, *Z. physik. Chem.*, **37**, 257 (1901).

[149] I. M. Kolthoff, *Z. anal. Chem.*, 60, 400 (1921); cf. V. Rothmund and A. Burgstaller, *Monatsh.*, **34**, 693 (1913).

[150] Cf. H. Menzel, *Z. physik. Chem.*, **105**, 424 (1923).

[151] E. Rupp and J. Mielck, *Arch. Pharm.*, **245**, 5 (1907).

[152] J. Mattner and R. Mattner, *Z. anal. Chem.*, **134**, 1 (1951).

Procedure: Dissolve, in a dry flask filled with nitrogen, 150–200 mg. of sample with 15 ml. of 30 per cent sodium hydroxide solution and 100 ml. of water. Add 20 ml. of 20 per cent potassium iodide solution and 25 ml. of concentrated hydrochloric acid. Titrate with standard sodium thiosulfate solution.

Manganese Dioxide: (*a*) Diehl[153] treated finely powdered manganese dioxide directly with potassium iodide and hydrochloric acid in the cold and titrated the liberated iodine:

$$MnO_2 + 4H^+ + 2I^- \longrightarrow I_2 + Mn^{2+} + 2H_2O$$

Iron which is usually found in mineral manganese dioxide interferes in the determination. Rupp[154] advised acidification with phosphoric instead of hydrochloric acid when ferric iron was complexed. However, the manganese dioxide then requires a long time for complete dissolution, and the results are much too high because of atmospheric oxidation of hydriodic acid. Air must be removed before satisfactory results can be obtained. Correct values are obtained by the following method.

Procedure: To about 150 ml. of finely powdered manganese dioxide in a glass-stoppered flask add 20 ml. of 4*N* phosphoric acid. Add three portions of about 300 mg. of sodium bicarbonate to drive the air from the flask. Add 1–1.5 g. of potassium iodide, stopper the flask, and allow to stand with occasional shaking in darkness or diffuse daylight until the complete dissolution of the manganese dioxide. Titrate with 0.1*N* thiosulfate solution.

(*b*) Distillation method of Bunsen. Bunsen[155] determined the higher oxides of manganese by distillation with strong hydrochloric acid, collection of the chlorine formed in a solution of potassium iodide, and titration of the liberated iodine. Carbon dioxide or hydrogen can be led through the distillation apparatus before and during the distillation. The method of Bunsen will only give exact results by painstaking attention to the various instructions.

Rupp[156] maintained that the chlorine formed in the distillation was reduced slightly by steam to hydrochloric acid so that the results were 0.5–2 per cent low. Kolthoff could not confirm this, but the method is difficult to carry out because of the ease with which the absorption solution sucks back into the distillation flask and because of the high hydrochloric acid content of the latter solution.

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[153] W. Diehl, *Dinglers Polytech. J.*, **246**, 196 (1882).

[154] E. Rupp, *Arch. Pharm.*, **254**, 135 (1916).

[155] R. Bunsen, *Ann.*, **86**, 265 (1853).

[156] E. Rupp, *Z. anal. Chem.*, **57**, 226 (1918); *Chem. Ztg.*, **43**, 423 (1928); G. Jander, *Z. anorg. Chem.*, **133**, 46 (1924).

Farsoe[157] modified the Bunsen method; he used 1–2 g. of potassium bromide, 20 ml. of concentrated sulfuric acid, and 80 ml. of water; the bromine produced was driven into the potassium iodide by a stream of carbon dioxide. There is some danger of iodine being lost from the solution by the passage of carbon dioxide.

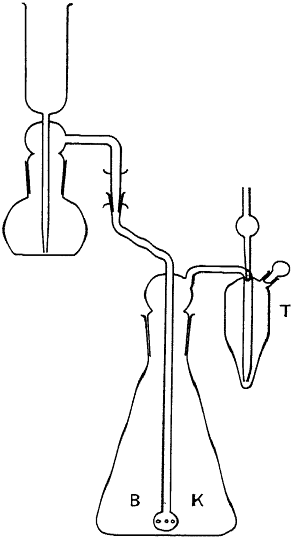

Fig. 1. Distillation apparatus of Rogers and Krieger.[158]

Rogers and Krieger[158] found similar results for the distillation with hydrochloric acid and hydrobromic acid. These authors recommended the apparatus which is shown in Fig. 1, which is entirely made of glass. The chlorine or bromine is collected in potassium iodide solution (BK) and, to avoid any losses of iodine, potassium iodide is also placed in the vessel T.

Various modifications of the Bunsen apparatus have been proposed; the original papers should be consulted for details. Hahn[159] altered the apparatus on the basis of the following considerations. Large amounts of hydrochloric acid should be avoided because, especially in the receiver, iodine can be liberated by atmospheric oxidation in strong acid solutions. Because of this, an indifferent vaporizing material should be used to drive over the chlorine and to dissolve the iodine and reduce its vapor pressure; carbon tetrachloride is suitable. The apparatus is constructed so that sucking back of the absorption solution is impossible, and the iodine liberated can be titrated in the same vessel; the distillate is cooled by a water condenser. Other forms of the Bunsen apparatus have been described by Parker and Robinson[160] and by Le Blanc and Eberius.[161] The latter authors found that the modified Bunsen method gave very exact results for the analysis of higher lead and manganese oxides. According to Lunge-Berl[162] the best procedure is to place excess of a bicarbonate solution of $0.1N$ arsenious acid in the absorber. This cannot be affected by the passage of carbon dioxide and, after the distillation, the solution is back-titrated with $0.1N$ iodine. The determination can thus be carried out quickly and cooling is unnecessary. Kolthoff found that the back-titration of excess arsenious oxide can also be done, after distillation in strong hydrochloric acid solution, with potassium bromate, using methyl red as indicator (see p. 506).

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[157] V. Farsoe, *Z. anal. Chem.*, 46, 308 (1907).

[158] K. B. Rogers and K. A. Krieger, *Ind. Eng. Chem., Anal. Ed.*, 5, 342 (1933).

[159] F. L. Hahn, *Ber.*, 63, 579 (1930).

(*c*) The difficulties normally associated with the direct iodometric method can be easily overcome by the use of ethylenediamine tetraacetic acid (EDTA); ferric iron does not interfere.[163]

Procedure: To approximately 50 mg. of sample in a glass-stoppered flask add a freshly prepared solution of a ten-fold amount (0.5 g.) of potassium iodide followed by 10 ml. of $0.1M$ EDTA, 0.5 g. of sodium acetate, and 10 ml. of 5 per cent acetic acid. Stir fairly slowly with an electromagnetic stirrer which has a heavy core (at low revolutions, this effectively grinds the undissolved oxide and frees its surface from the lead iodide formed); dissolution should be complete in 15–20 minutes. When all the oxide has dissolved, rinse the stopper, dilute slightly, and titrate the liberated iodine with 0.05–$0.1M$ thiosulfate.

Notes: (1) If dissolution was incomplete, the color of the solution returns. The solution should then be allowed to stand for some time before further titration. The initial sample should be thoroughly ground in an agate mortar. Rapid dissolution of the initial sample may also be achieved by using a thick-walled flask and glass beads to form a layer on the bottom; the sample dissolves on shaking for 2–5 minutes.

(2) Ferric iron may be determined in the presence of manganese dioxide by repeating the above procedure without adding EDTA; the amount of iron is found by difference.

Lead Dioxide: Pamfilov[164] has investigated iodometric methods for the determination of lead dioxide. The method of the Bureau of Standards[165] gives good, reproducible results. In stronger acid solution, the method of Glasstone[166] gives excellent results.

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[160] T. W. Parker and P. L. Robinson, *J. Chem. Soc.*, **1929**, 1106.

[161] M. LeBlanc and E. Eberius, *Z. anal. Chem.*, **89**, 81 (1932).

[162] G. Lunge and E. Berl, *Chem.-tech. Unters. Meth.*, 7Aufl. 1, 972 (1921).

[163] R. Přibil and J. Čihalík, *Collection Czech Chem. Communs.*, **20**, 562 (1955).

[164] A. V. Pamfilov, *Z. anal. Chem.*, **78**, 40 (1929).

[165] *Natl. Bur. Standards U.S. Circ.* 90.

[166] S. Glasstone. *J. Chem. Soc.*, **119**, 1997 (1921).

Lead Dioxide, Red Lead, Manganese Dioxide: Pamfilov and Ivančeva[167] used the method of Rupp and Siebler,[168] which is said to give very good results.

Procedure: To 0.1–0.2 g. of the dioxide or 0.5 g. of red lead, add 25 ml. of 0.1*N* neutral solution of arsenious oxide and 10 ml. of 5*N* hydrochloric acid. Shake until the substance has mostly dissolved. Boil under reflux (because of volatility of arsenic trichloride) for 15 minutes to dissolve all the larger particles. The excess of arsenious acid is titrated with bromate (p. 506).

Lead dioxide may also be determined by a procedure similar to that used for manganese dioxide in which EDTA is used to complex ferric iron (p. 286).[163] Although dissolution is rapid at high concentrations of acetic acid, the results tend to be low; in neutral or faintly acid solution, good results are obtained but the reaction is rather slow. The optimum range is 10–20 ml. of 5 per cent acetic acid for 50–100 ml. of solution.

The EDTA must be added after the iodide, for otherwise it is oxidized by lead dioxide.

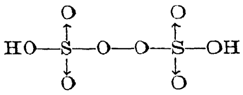
Procedure: Follow the procedure for manganese dioxide (p. 286) but use the following quantities (the figures in parentheses indicate the amounts for semimicro work). To 0.2 g. (0.03–0.05 g.) of finely ground sample, add a solution of 1.5–2 g. (0.5 g.) of potassium iodide, 10–15 ml. (2–5 ml.) of 0.1*M* EDTA and 10 ml. (5 ml.) of 5 per cent acetic acid. Continue as described on p. 286.

Note: Lead(II) oxide may be determined after the iodometric titration if a known excess of EDTA is added in the procedure. The solution is neutralized to methyl orange with ammonia, 2 ml. of buffer (54 g. of ammonium chloride and 350 ml. of 25 per cent ammonia per liter) is added, and the excess of EDTA is titrated against 0.1*M* magnesium sulfate with eriochrome black as indicator. This gives the total amount of lead. If other cations, e.g., copper, zinc, are present, a little cyanide is added before the back-titration.

Peroxydisulfate: In acid solution, peroxydisulfate reacts very slowly with potassium iodide, especially if the solution is dilute.

$$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$$

The slow rate of reaction is common to those peroxides in which the peroxy group is bound up in the molecule; cf. acetyl peroxide, peroxydiphosphate, and benzoyl peroxide.



$$HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-O-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-OH$$

Taube[169] investigated the mechanism of the peroxydisulfate-iodide reaction and concluded that in contrast to the hydrogen peroxide–iodide reaction which proceeds via HOI formation, this reaction proceeds through the formation of monatomic iodine.

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[167] A. V. Pamfilov and E. G. Ivančeva, *Z. anal. Chem.*, 88, 23 (1932).

[168] E. Rupp and G. Siebler, *Chem. Ztg.*, 48, 241 (1924).

[169] H. Taube, *J. Am. Chem. Soc.*, 64, 161 (1942).

$$I^- + S_2O_8^{2-} \longrightarrow I + S_2O_8^{3-} \quad (\text{or } SO_4^{2-} + SO_4^-)$$

Another possible mechanism involves the following reactions:

$$I^- + S_2O_8^{2-} \xrightarrow{k} S_2O_8I^{3-} \qquad (\text{rate-determining})$$

$$S_2O_8I^{3-} = S_2O_8^{3-} + I$$

$$S_2O_8^{3-} + I^- = 2SO_4^{2-} + I$$

$$S_2O_8I^{3-} + H_2O = 2SO_4^{2-} + HOI + H^+$$

The peroxydisulfate-iodide reaction is accelerated by higher temperatures and by a large excess of iodide. Mondolfo[170] heated peroxydisulfate with potassium iodide in a glass-stoppered flask for 5–10 minutes at 60–80°C. and, after cooling the solution, titrated it with thiosulfate. According to Schwicker,[171] the reaction is complete in a reasonable time at room temperature if enough potassium iodide is added to the neutral solution. Müller and Ferber[172] used ferrous salts to catalyze the reaction, but large amounts of iodide must still be used. Kiss and Bruckner[173] studied extensively the rate of reaction of peroxydisulfate and iodide and established that an increase in the ionic strength of the medium greatly accelerated the reaction; of the 23 neutral salts tested, potassium chloride was the most effective. Hydrogen ion had no specific catalytic effect; a strong mineral acid gave about the same effect as a neutral salt. Kolthoff and Carr[174] investigated critically the iodometric and ferrometric methods for the determination of peroxydisulfate in both the presence and the absence of organic substances. Good results are obtained by the following procedure in solutions having pH values from 7 to 0.2. Unless organic substances oxidize iodide or react with iodine, the iodometric method is more convenient than the ferrometric method and yields excellent results.

Procedure: Introduce into a 125 ml. iodine flask a measured amount of sample containing the equivalent of 5–500 mg. of potassium peroxydisulfate. Dilute the solution to about 30 ml., add 4 g. of potassium iodide, stopper the flask, swirl to dissolve the iodide, and then allow to stand for 15 minutes.

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[170] G. H. Mondolfo, *Chem. Ztg.*, **23**, 699 (1899).

[171] A. Schwicker, *Z. anal. Chem.*, **74**, 433 (1928).

[172] E. Müller and H. von Ferber, *Ber.*, **38**, 3965 (1906).

[173] A. von Kiss and V. Bruckner, *Z. physik. Chem.*, **128**, 71 (1927).

[174] I. M. Kolthoff and E. M. Carr, *Anal. Chem.*, **25**, 298 (1953).

Acidify the solution with 1–2 ml. of 6 N acetic acid and titrate it with standard 0.01N or 0.1N thiosulfate to the starch end-point.

Notes: (1) Large amounts of electrolyte, especially iodide, adversely affect the sharpness of the end-point.

(2) Half the amount of potassium iodide specified in the procedure may be used if the reaction mixture is allowed to stand for 45 minutes before titration with thiosulfate.

(3) To avoid air-oxidation of iodide, oxygen should be removed from the solution before adding the iodide by adding several small portions of sodium bicarbonate.

(4) Organic substances which neither react with iodine nor reduce iodide do not interfere in concentrations up to 1M. Methanol, ethanol, and acrylonitrile do not interfere. Allyl acetate, acetone, and formaldehyde introduce errors of the order of 1 per cent. Acetone reacts with iodine to form monoiodoacetone:

$$CH_3COCH_3 + I_2 \rightleftharpoons ICH_2COCH_3 + HI$$

Since the reaction is reversed by acid, the error introduced by acetone may be reduced by adding 2 ml. of 1:1 sulfuric acid to the solution after the peroxydisulfate-iodide reaction is complete. In the determination of 32 mg. of potassium peroxydisulfate in 1.8M acetone solution, the result was 3.3 per cent low by the general procedure but only 0.6 per cent low when the procedure was modified by adding 2 ml. of 1:1 sulfuric acid.

(5) The determination of peroxydisulfuric acid, peroxymonosulfuric acid, and hydrogen peroxide in the presence of each other has also been studied extensively by Schulek and his coworkers.[175]

According to Müller,[176] peroxydisulfate quantitatively oxidizes iodide to iodate in alkaline medium.

$$3S_2O_8^{2-} + I^- + 6OH^- \longrightarrow 6SO_4^{2-} + IO_3^- + 3H_2O$$

If the solution is then acidified with dilute sulfuric acid, the iodate reacts with iodide in the usual way.

The overall process is expressed by the equation

$$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$$

Procedure: To an Erlenmeyer flask add 25 ml. of 2N sodium hydroxide and 2 g. of potassium iodide. After the iodide dissolves, add the solution of peroxydisulfate. The solution must remain alkaline (provision for this must be made, for example, in the analysis of acid solutions). Heat the solution to a gentle boil on a hot plate and boil for 3 minutes. After the solution is cool, acidify with 15 ml. of 4N sulfuric acid and titrate with standard thiosulfate solution.

Notes: (1) Kurtenacker[177] obtained very good results with the above procedure when substances which reduce hypoiodite were absent. Among interfering substances are organic materials, ammonium salts, and hydrogen peroxide. The method is not recommended for the analysis of ammonium persulfate or solutions containing ammonium salts. If the solution contains hydrogen peroxide, it is possible to titrate the former with ceric or permanganate and determine the peroxydisulfate in the hydrogen peroxide-free solution.

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[175] E. Schulek, E. Pungor, and J. Trompler, *Acta Chim. Acad. Sci. Hung.*, **4**, 393, 405, 411, 417, 423 (1954).

[176] E. Müller and H. von Ferber, *Z. anal. Chem.*, **52**, 195 (1913); E. Müller, *Z. anal. Chem.*, **52**, 299 (1913).

[177] A. Kurtenacker, *Z. anal. Chem.*, **88**, 171 (1932).

(2) Van der Meulen[178] recommends the use of a smaller excess of sodium hydroxide. Heat on a water bath a mixture of 50 ml. of peroxydisulfate solution (*ca.* 0.1*N*), 6–7 ml. of *N* sodium hydroxide, and 10 ml. of *N* potassium iodide, acidify it and titrate the liberated iodine with standard thiosulfate. The iodide and sodium hydroxide must be pure in order to obtain good results. It is recommended that a blank determination be run using a measured amount of iodine, the potassium iodide, and the sodium hydroxide to test the reagent.

5. Sulfur and Sulfur Compounds. ***Elemental Sulfur:***[179] The iodometric determination of elemental sulfur generally involves the reduction of sulfur to sulfide followed by the iodometric titration of the sulfide.

Elemental sulfur suspended in water is reduced to hydrogen sulfide by zinc, aluminum, or iron in the presence of hydrochloric acid. Comay[180] used iron powder previously reduced with hydrogen, and collected the evolved hydrogen sulfide in ammoniacal cadmium chloride solution. The sulfide in this solution was determined by acidifying the solution and titrating with standard iodine solution. Guppy[181] used tin in the presence of hydrochloric and acetic acids to reduce sulfur to hydrogen sulfide.

Hardman and Barbehenn[182] in the analysis of rubbers observed that sulfur dissolves in acetone quickly and reacts quantitatively with a clean copper surface to form cuprous sulfide. The copper gauze with cuprous sulfide is rinsed carefully to prevent scaling of the sulfide, transferred to a gas evolution flask, and treated with concentrated hydrochloric acid. The evolved hydrogen sulfide gas is collected in ammoniacal cadmium chloride solution. The mixture is treated with an excess of standard iodide–iodate solution, acidified with hydrochloric acid, and back-titrated with standard thiosulfate solution. Levin and Stehr[183] modified the procedure slightly for the determination of sulfur in petroleum oils and describe a convenient apparatus. Acetone exerts an apparent catalytic effect on the reaction of sulfur with copper and is used as solvent. No sulfur is lost in the procedure, hydrogen sulfide and other sulfur compounds in petroleum do not interfere, and good results are obtained on a variety of samples.

A method for the determination of elemental sulfur in rubber based on its reaction with sulfite to form thiosulfate

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[178] J. H. van der Meulen, *Z. anal. Chem.*, **88**, 173 (1932).

[179] For a review of earlier studies on the estimation of sulfur, see F. H. Garner and E. B. Evans, *J. Inst. Petroleum Technol.*, **17**, 451 (1931).

[180] S. Comay, *Ind. Eng. Chem., Anal. Ed.*, **8**, 460 (1936).

[181] W. D. Guppy, *Trans. Inst. Rubber Ind.*, **7**, 81 (1931); *Chem. Abstr.*, **26**, 624 (1932).

[182] A. F. Hardman and H. E. Barbehenn, *Ind. Eng. Chem., Anal. Ed.*, **7**, 103 (1935).

[183] H. Levin and E. Stehr, *Ind. Eng. Chem., Anal. Ed.*, **14**, 107 (1942).

$$SO_3^{2-} + S \longrightarrow S_2O_3^{2-}$$

is described by Bolotnikov and Gurova.[184] Excess sulfite is removed with formaldehyde and the thiosulfate titrated iodometrically in an acetic acid solution. Oldham, Baker, and Craytor[185] improved the method by using sodium stearate to assist in the extraction of sulfur, removing mercaptans with cadmium acetate, diluting the solution before titration, and cooling to improve the end-point stability. Morris, Lacombe, and Lane[186] use a similar procedure for the determination of free sulfur in aromatic hydrocarbons. Their procedure is accurate to within 1–2 per cent of the true sulfur content down to a concentration of 0.1 per cent. They report that thiophene, thiophenol, and other sulfur compounds do not interfere, although no data are presented to substantiate this. (It is interesting that mercaptans and hydrogen sulfide which react with iodine do not interfere. They are probably volatilized in the procedure.)

The original papers should be consulted for details of these methods.

Hydrogen Sulfide and Sulfides: Hydrogen sulfide is oxidized by iodine according to the equation

$$H_2S + I_2 \longrightarrow S + 2H^+ + 2I^-$$

Many contradictions appear in the literature regarding the accuracy of the iodometric determination of hydrogen sulfide.[187] Kolthoff[188] systematically investigated the method and found that, in alkaline solution, part of the sulfide is oxidized to sulfate:

$$S^{2-} + 4I_2 + 8OH^- \longrightarrow SO_4^{2-} + 8I^- + 4H_2O$$

Even in a weakly alkaline solution of bicarbonate this reaction is appreciable. To obtain accurate results with even very dilute solutions, the solution of sulfide may be added from a burette to an acid iodine solution until the blue starch-iodine color disappears, or the sulfide solution may be pipetted into an excess of acid iodine solution which is back-titrated with thiosulfate. The sulfur which separates does not interfere in the determination. If a weakly acid solution of sulfide is titrated directly with iodine solution, some hydrogen sulfide may be lost by volatilization unless some precautions (e.g., use of special titration flasks, such as are mentioned on p. 502) are taken. Very dilute solutions of hydrogen sulfide may be titrated directly without loss. Some of the errors in the iodometric determination of hydrogen sulfide and sulfides are discussed by Bethge.[189]

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[184] V. Bolotnikov and V. Gurova, *J. Rubber Ind.* (*U.S.S.R.*), **10**, 61 (1933); *Chem. Abstr.*, **28**, 4934 (1934).

[185] E. W. Oldham, L. M. Baker, and M. W. Craytor, *Ind. Eng. Chem., Anal. Ed.*, **8**, 41 (1936).

[186] H. E. Morris, R. E. Lacombe, and W. H. Lane, *Anal. Chem.*, **20**, 1037 (1948).

[187] Cf. O. Brunck, *Z. anal. Chem.*, **45**, 541 (1906).

[188] I. M. Kolthoff, *Z. anal Chem.*, **60**, 451 (1921).

Bromine (bromate-bromide-acid mixture; cf. p. 529) or hypobromite (p. 587) quantitatively oxidizes sulfide to sulfate. Since sulfite is oxidized to sulfate by both iodine and bromine, it is possible to determine sulfide and sulfite in the presence of each other.

Bethge,[190] who examined several methods for the determination of hydrogen sulfide and soluble sulfides, including oxidation with iodine, concluded that the best oxidant is potassium iodate in an alkaline medium because of its greater stability. Sulfide is oxidized to sulfate.

Procedure: Mix 10 ml. of the sulfide solution containing about 2.5 mg. of sulfide with 15 ml. of $0.1N$ potassium iodate solution and 10 ml. of $10N$ sodium hydroxide. Boil gently for 10 minutes, cool, add 5 ml. of 5 per cent potassium iodide solution and 20 ml. of $8N$ sulfuric acid. Titrate the liberated iodine, which represents the unconsumed iodate, with $0.1N$ sodium thiosulfate.

Note: Oxidation at room temperature gives a yield of only 95 per cent. When the alkali concentration is $3.5N$, quantitative oxidation is still obtained when the solution is boiled for 10 minutes; at $1N$, however, the recovery is only 98 per cent.

The iodometric titration of sulfide is useful for the determination of metals, such as zinc, cadmium, mercury, and lead, which are precipitated as sulfides, separated, washed, and titrated iodometrically.

For the determination of polysulfide in the presence of sulfide, see the comprehensive work of Bodnár and Gervay.[191] The most satisfactory method for the determination of polysulfide is that of Schulek[192] in which polysulfide is converted to thiocyanate with alkali metal cyanide in the presence of boric acid. Sulfide is boiled out as hydrogen sulfide and collected in the distillate, and the thiocyanate remaining is determined iodometrically (see p. 307).

Sulfates: St. Lorant[193] found that sulfate is quantitatively reduced to hydrogen sulfide on boiling with hydrogen iodide and phosphorus and formic acid. Luke[194] investigated this method and described a determination of sulfate by reduction with hydrogen iodide

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[89] P. O. Bethge, *Anal. Chim. Acta*, **9**, 129 (1953); **10**, 113 (1954).

[90] P. O. Bethge, *Anal. Chim. Acta*, **10**, 310 (1954).

[91] J. Bodnár and W. Gervay, *Z. anal. Chem.*, **71**, 446 (1927).

[92] E. Schulek, *Z. anal. Chem.*, **65**, 352 (1925).

[93] St. Lorant, *Z. physiol. Chem.*, **185**, 245 (1929).

[94] C. L. Luke, *Ind. Eng. Chem., Anal. Ed.*, **15**, 602 (1943).

and hypophosphorous acid and iodometric titration of the sulfide. He applied the method to the determination of total sulfur in rubber.

Sulfurous Acid and Its Salts: The iodometric determination of sulfurous acid and its salts is based on the reaction

$$SO_3^{2-} + I_2 + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2I^-$$

Many contradictions appear in the literature concerning the iodometric titration of sulfite. The principal sources of error are the oxidation of sulfurous acid by air and the loss of sulfur dioxide by volatilization.[195] Air-oxidation of sulfite is especially rapid in alkaline solutions, and to reduce errors Ruff and Jeroch[195] suggest the use of mannitol, which acts as a negative catalyst.

According to Raschig,[195] accurate results in the iodometric determination of sulfite are obtained only when the sulfite solution is allowed to flow from a pipette into an excess of standard iodine solution. On the basis of his investigations, Kolthoff[196] recommends this procedure. It is not necessary, however, to pipette the sulfite solution under the iodine solution; the sulfite may be added to an excess of iodine solution in the usual manner and the iodine back-titrated with thiosulfate. Alternatively, the sulfite solution may be used as titrant and added directly from a burette to a measured amount of standard iodine solution until the latter is completely decolorized, starch being used as indicator. The direct titration of sulfurous acid or its salts with iodine in the burette always gives incorrect results even if catalysts negative to air-oxidation, e.g., mannitol, cane sugar, and alcohol, are present.

If other reducing agents are present with sulfite, it is possible to titrate iodometrically a portion of the sample in order to determine the total equivalents of reducing agents. A second portion is then titrated after deactivating sulfite with formaldehyde or acetone.[197] The difference in titer corresponds to the sulfite present in the sample. This method was used by Prater *et al.*[198] for the determination of sulfur dioxide in dehydrated foods. They observed that sulfur dioxide combines with glucose syrup solution, e.g., fruit juices, foods, and wines, and is not titrated completely by direct iodometric titrations.[199] The sulfur dioxide in these solutions may be liberated by treatment with sodium hydroxide and then titrated iodometrically immediately after acidification with sulfuric acid.

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[195] F. Raschig, *Z. angew. Chem.*, **17**, 577 (1904); O. Ruff and W. Jeroch, *Ber.*, **38**, 409 (1905); H. M. Mason and G. Walsh, *Analyst*, **53**, 142, 144 (1928).

[196] I. M. Kolthoff, *Z. anal. Chem.*, **60**, 448 (1921).

[197] Cf. A. Kurtenacker, *Z. anal. chem.*, **64**, 56 (1924).

[198] A. N. Prater, C. M. Johnson, M. F. Poole, and G. MacKinney, *Ind. Eng. Chem., Anal. Ed.*, **16**, 153 (1944).

Thiosulfate: The iodometric titration of thiosulfate has already been discussed extensively (p. 213). In neutral and even in bicarbonate solutions, the reaction proceeds stoichiometrically according to the equation

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

In solutions of high alkalinity, thiosulfate is oxidized quantitatively to sulfate by excess iodine:

$$S_2O_3^{2-} + 4I_2 + 10OH^- \longrightarrow 2SO_4^{2-} + 8I^- + 5H_2O$$

Abel[200] used this reaction for the determination of thiosulfate. Kolthoff[201] found the following procedure suitable.

To 25 ml. of approximately $0.01M$ thiosulfate solution add 10 ml. of N sodium hydroxide and 25 ml. of standard $0.1N$ iodine. Allow the solution to stand 5 minutes, acidify with sulfuric acid and titrate the excess iodine with standard $0.1N$ thiosulfate solution.

Silver Chloride: Haslewood[202] uses the iodometric titration of thiosulfate for the determination of silver chloride. If 4 ml. of glacial acetic acid is added to 2.5 mg. of silver chloride dissolved in 1 ml. of $0.2N$ sodium thiosulfate solution, an amorphous precipitate ($Na_5Ag(S_2O_3)_4 \cdot 2H_2O$)[203] forms which rapidly crystallizes in fine needles. The precipitate is washed with glacial acetic acid, dissolved in excess standard $0.01N$ iodine solution, and back-titrated with standard $0.005N$ thiosulfate solution with very little loss of silver. The solubility of the precipitate corresponds to 3 mg. of AgCl per liter.

Mixture of Sulfide, Sulfite, and Thiosulfate:[204] This analysis was investigated thoroughly by Kurtenacker and Wollak.[205] They removed sulfide from a solution of the sample as zinc or cadmium sulfide. When zinc or cadmium salt solution is used as precipitant, the voluminous sulfide precipitate formed strongly coprecipitates other ions. If a freshly prepared suspension of zinc or cadmium carbonate is used, a coarse sulfide precipitate is formed which does not coprecipitate sulfite and thiosulfate. Zinc and cadmium carbonates are equally effective, but the former is generally used. If the solution contains 5 per cent of glycerin (glycerol) or alcohol to retard the air-oxidation of sulfite, it is possible simply to filter the solution after the precipitation of sulfide and determine sulfite and thiosulfate iodometrically in the filtrate. The sum of these is determined in a portion of filtrate. An excess of formaldehyde is added to a second portion of filtrate to bind sulfite as the inert aldehyde bisulfite compound and the thiosulfate is titrated iodometrically after acidifying with acetic acid.

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[199] Cf. G. W. Monier-Williams, *Reports on Public Health and Medical Subjects*, No. 43, Ministry of Health, H. M. Stationery Office, London, 1927; *Analyst*, 52, 343 (1927); H. R. Jensen, *ibid.*, 53, 133 (1928); A. H. Bennett and F. K. Donovan, *ibid.*, 68, 140 (1943).

[200] E. Abel, *Z. anorg. Chem.*, 74, 395 (1912).

[201] I. M. Kolthoff, *Z. anal. Chem.*, 60, 341 (1921).

[202] G. A. D. Haslewood, *J. Chem. Soc.*, 1936, 1049.

[203] Cf. H. Bassett and J. T. Lemon, *J. Chem. Soc.*, 1933, 1423.

[204] A complete and excellent review of the analytical methods for the detection and determination of oxygen acids of sulfur and their corresponding salts is given by A. Kurtenacker, *Analytische Chemie der Sauerstoffsauren des Schwefels*, Vol. XXXVIII in the series *Die chemisches Analyse*, W. Bottger, ed., Enke, Stuttgart, 1938.

[205] A. Kurtenacker and R. Wollak, *Z. anorg. u. allgem. Chem.*, 161, 201 (1927); cf. A. Kurtenacker and K. Bittner, *ibid.*, 141, 297 (1924); Ref. 204, p. 127.

The sulfide is determined directly by adding the washed zinc or cadmium sulfide precipitate to an excess of acidified iodine solution and back-titrating with thiosulfate solution. Alternatively, a portion of the original sample is added to an excess of acidified iodine solution and back-titrated with thiosulfate solution. This titration determines the sum of sulfide, sulfite, and thiosulfate from which the amount of sulfide is determined by difference.

Reagent: Prepare a solution of 40 g. of $ZnSO_4 \cdot 7H_2O$ in 200 ml. of water and another of 20 g. of Na_2CO_3 in 200 ml. of water. A fresh zinc carbonate suspension is prepared as needed by mixing at room temperature with rapid stirring 20 ml. of zinc solution with 20 ml. of carbonate solution; this amount is sufficient for the precipitation of 20–30 ml. of 0.4*N* sodium sulfide.

Procedure: (*a*) Transfer a measured portion of sample solution[206] to a 250 ml. volumetric flask. Add 15 ml. of glycerol or alcohol, dilute to approximately 150 ml. with water, and add 20 ml. of fresh zinc carbonate suspension to precipitate the sulfide (if much sulfide is present more zinc carbonate suspension must be used). Dilute the solution to the mark with water and mix thoroughly. Filter through a dry filter paper.

Treat an aliquot portion of filtrate with 5 ml. of 35–40 per cent formaldehyde; then acidify with 20 ml. of 10 per cent acetic acid and titrate immediately with standard 0.1*N* iodine solution to the starch end-point. The titer corresponds to the thiosulfate content of the sample.

Pipette a second aliquot of the filtrate into an excess of acidified standard iodine solution and back-titrate with standard thiosulfate solution. The net titer of iodine is equivalent to the sum of the thiosulfate and sulfite in the solution.

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[206] Solid samples are dissolved in 5 per cent glycerol or alcohol rather than water. Aliquot portions of such solutions may be used for analysis.

(*b*) To determine the sum of sulfide, sulfite, and thiosulfate in the sample, pipette a measured amount of original sample solution into an excess of acidified standard iodine solution and back-titrate with standard thiosulfate solution. The sulfide content of the sample is determined by difference.

Alternatively, the sulfide content may be determined directly in the precipitate removed in (*a*). Wash the precipitate with water, transfer with the paper to an excess of acidified standard iodine solution, and back-titrate with standard thiosulfate solution.

Note: Karchmer and Dunahoe[207] use this procedure for a rapid analysis of refinery spent caustic solution. The procedure is modified slightly if mercaptans are present. Uhrig and Levin[208] apply the method to the determination of thiosulfate in used "doctor" solution (doctor solution is sodium plumbite in an excess of sodium hydroxide). A diluted sample solution is treated with carbon dioxide gas until the pink color of phenolphthalein is discharged, and then for 5 minutes longer. The lead is precipitated and the sulfite is converted to bisulfite. To the filtrate add an excess of formaldehyde and, after 5 minutes standing, 10 per cent acetic acid. Titrate the thiosulfate with standard iodine solution, using starch as indicator.

Wollak[209] devised a modified procedure for the determination of sulfide, sulfite, and thiosulfate.

Procedure: (*a*) Determine the sum of sulfide, sulfite, and thiosulfate as in the above procedure.

(*b*) To determine sulfide and thiosulfate, add a portion of sample solution to a 500 ml. iodine flask, treat with 15 ml. of 10 per cent zinc acetate solution, and dilute with water to approximately 150 ml. Without removing the precipitate, add 5 ml. of 35–40 per cent formaldehyde, acidify with 20 ml. of 10 per cent acetic acid, add an excess of standard $0.1N$ iodine solution and back-titrate with standard thiosulfate solution.

(*c*) To determine thiosulfate, add a third portion of sample solution slowly to a 500 ml. iodine flask containing an excess of weakly acid (approximately $0.1N$ sulfuric acid) iodine solution (approximately $0.2N$) and titrate the excess iodine carefully to the starch end-point with approximately $0.1N$ sulfite solution. Make the solution alkaline to methyl red with approximately $0.1N$ ammonia. Add 7 ml. of 10 per cent potassium cyanide solution and allow to stand for 10–15 minutes. After this period, acidify the solution with 25–50 ml. of $6N$ sulfuric acid and titrate to the first permanent blue color with standard iodine solution. The equivalents of iodine used in this titration correspond to half the number of moles of thiosulfate in the solution.

Note: The above thiosulfate procedure is explained as follows. In the beginning, thiosulfate is oxidized to tetrathionate by iodine, whereas sulfide is oxidized to sulfur, and sulfite to sulfate. In neutral or weakly alkaline solution, tetrathionate reacts with potassium cyanide according to the equation:[210]

$$3KCN + Na_2S_4O_6 + H_2O \longrightarrow Na_2S_2O_3 + K_2SO_4 + KSCN + 2HCN$$

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[207] J. H. Karchmer and J. W. Dunahoe, *Anal. Chem.*, **20**, 915 (1948).

[208] K. Uhrig and H. Levin, *Ind. Eng. Chem., Anal. Ed.*, **14**, 547 (1942).

[209] R. Wollak, *Z. anal. Chem.*, **77**, 401 (1929).

[210] A. Kurtenacker and A. Fritzsch, *Z. anorg. u. allgem. Chem.*, **117**, 202, 262 (1921).

After the solution is acidified, the thiosulfate produced from the tetrathionate is titrated iodometrically. For each mole of thiosulfate originally present in the sample solution, only half a mole is re-formed. For a further discussion of details in the procedure, see p. 298 for the determination of polythionates.

Mixture of Hyposulfite (Dithionite), Sulfite, and Thiosulfate: Hyposulfite is oxidized quantitatively to sulfate by iodine.[211]

$$S_2O_4^{2-} + 3I_2 + 4H_2O \longrightarrow 2SO_4^{2-} + 6I^- + 8H^+$$

However, the direct titration is of no practical value since sulfite, which is always present with hyposulfite, also reacts. This interference can be eliminated by the addition of an excess of formaldehyde which reacts with hyposulfite to form formaldehyde bisulfite and formaldehyde sulfoxylate.

$$S_2O_4^{2-} + 2HCHO + H_2O \longrightarrow HCHO{\cdot}HSO_3^- + HCHO{\cdot}HSO_2^-$$

Formaldehyde bisulfite is inert to iodine, whereas the sulfoxylate reacts readily according to the equation

$$HCHO{\cdot}HSO_2^- + 2I_2 + 2H_2O \longrightarrow SO_4^{2-} + HCHO + 4I^- + 5H^+$$

The solution treated with formaldehyde is very stable toward air-oxidation, so the titration may be carried out in an open vessel. Wollak[212] used the following procedure for the analysis of a mixture of hyposulfite, sulfite, and thiosulfate.

Procedure. (*a*) Hyposulfite and Thiosulfate: To 1 g. of sample in a glass-stoppered tube add 10 ml. of 35–40 per cent formaldehyde (neutral to methyl orange) and 5 ml. of water. Stopper the tube and allow the solution to stand for 20 minutes. Transfer the solution to a 500 ml. volumetric flask and dilute to volume with water. To a 50 ml. aliquot portion of this solution add 2 drops of phenolphthalein indicator solution. If the solution is alkaline, acidify with 20 per cent acetic acid. Dilute to 200 ml., add an excess of standard iodine solution, and back-titrate with standard thiosulfate solution. The net iodine titer corresponds to the sum of hyposulfite and thiosulfate.

(*b*) Thiosulfate: Tetrathionate reacts quantitatively with sulfite in neutral solution according to the equation[213]

$$S_4O_6^{2-} + SO_3^{2-} \longrightarrow S_3O_6^{2-} + S_2O_3^{2-}$$

The optimum pH range is from 5.5 to 9.5, within which range the reaction is quantitative in 5 minutes.

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[211] A. Bernthsen, *Ann.* **208**, 162 (1881); *Ber.*, **14**, 440 (1881); M. Bazlen and A. Bernthsen, *Ber.*, **43**, 501 (1910).

[212] R. Wollak, *Z. anal. Chem.*, **80**, 1 (1930); cf. T. Murooka, *Bull. Inst. Phys.-Chem. Research* (*Tokyo*), **22**, 18 (1943); *Chem. Abstr.*, **31**, 6832 (1947).

[213] A. Kurtenacker, *Z. anorg. u. allgem. Chem.*, **134**, 265 (1924).

Add 0.2 g. of sample to an excess of iodine solution containing about 1 g. of sodium acetate. Shake to dissolve the sample, reduce the excess iodine with a 5 per cent sodium sulfite heptahydrate solution, and add 30 ml. in excess. Neutralize the solution to phenolphthalein with *N* sodium hydroxide and allow to stand for 5 minutes. Add 5 ml. of 35–40 per cent formaldehyde to bind the excess sulfite, acidify the solution with 10 ml. of 20 per cent acetic acid, and titrate with standard iodine solution. The iodine consumed corresponds to half of the thiosulfate originally present in the sample.

(*c*) Sulfite: Determine the sum of hyposulfite, sulfite, and thiosulfate in the sample by adding a portion of sample to an excess of standard iodine solution as in the procedure in (*b*), and back-titrate with standard thiosulfate solution. The sulfite content is calculated by difference.

Bisulfite, Thiosulfate, Sulfide , Tri- and Polythionates in Presence of One Another. Kurtenacker and Goldbach[214] devised a simpler, more reliable method than that previously used for the quantitative analysis of an aqueous solution containing bisulfite, thiosulfate, (under certain conditions, sulfide), tri-, tetra-, and pentathionate. Since sulfide and sulfite are usually not present together, the procedure is given for the analysis of a sulfide-free solution. If sulfide is present, the procedure is modified to remove the sulfide with zinc carbonate suspension; for full details, consult the original work. Five individual analyses are carried out on the solution, which is freed from elemental sulfur.

In a neutral solution, polythionates having more than three sulfur atoms react with alkali metal sulfite:[215]

$$S_6O_6^{2-} + 3SO_3^{2-} \longrightarrow S_3O_6^{2-} + 3S_2O_3^{2-}$$

$$S_5O_6^{2-} + 2SO_3^{2-} \longrightarrow S_3O_6^{2-} + 2S_2O_3^{2-}$$

$$S_4O_6^{2-} + SO_3^{2-} \longrightarrow S_3O_6^{2-} + S_2O_3^{2-}$$

The optimum pH for these reactions lies between 5.5. and 9.5. In this pH range, the reactions take place quantitatively at room temperature in a few minutes if an excess of sulfite is used. After the excess sulfite is bound with formaldehyde, the thiosulfate formed from the polythionates is titrated iodometrically; trithionate does not interfere. Naturally, the presence of sulfite in the sample does not interfere either.

Polythionates containing more than three sulfur atoms, when present in dilute aqueous solution, react quickly and quantitatively with alkali metal cyanide:

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[214] A. Kurtenacker and E. Goldbach, *Z. anorg. u. allgem. Chem.*, **166**, 177 (1927).

[215] A. Kurtenacker, *Z. anorg. u. allgem. Chem.*, **134**, 265 (1924).

$$S_6O_6^{2-} + 5CN^- + H_2O \longrightarrow S_2O_3^{2-} + SO_4^{2-} + 3SCN^- + 2HCN$$

$$S_5O_6^{2-} + 4CN^- + H_2O \longrightarrow S_2O_3^{2-} + SO_4^{2-} + 2SCN^- + 2HCN$$

$$S_4O_6^{2-} + 3CN^- + H_2O \longrightarrow S_2O_3^{2-} + SO_4^{2-} + SCN^- + 2HCN$$

These reactions take place quantitatively in neutral or weakly alkaline solutions in 1–2 minutes if the temperature is over 20° but require 10–15 minutes at 15°C. An acid solution must be neutralized before the analysis is carried out; strong alkalis decompose the polythionates to sulfite and thiosulfate, so neutralization should be effected with a weak base rather than sodium hydroxide. The cyanide-polythionate reactions take place quantitatively according to the above equations only in dilute solutions. In concentrated (e.g., *N*) polythionate solutions, cyanide reacts partially with the thiosulfate formed from the above reactions:

$$S_2O_3^{2-} + CN^- \longrightarrow SO_3^{2-} + SCN^-$$

introducing errors in the procedure.

Trithionate also reacts with cyanide:

$$S_3O_6^{2-} + 3CN^- + H_2O \longrightarrow SO_3^{2-} + SO_4^{2-} + SCN^- + 2HCN$$

but under the conditions used in the determination of higher polythionates the reaction is incomplete. Since sulfite rather than thiosulfate is formed in this reaction, the effect on the determination of the higher polythionates is readily nullified by the addition of formaldehyde.

According to Schmitt,[216] the end-point of the titration may be somewhat difficult to recognize since the blue color of starch disappears quickly at first but rather slowly later in the titration; it is necessary to titrate to the point where the blue color remains for at least 5 minutes.

Polythionates react with alkali metal sulfides according to the equation[217]

$$S_nO_6^{2-} + S^{2-} \longrightarrow 2S_2O_3^{2-} + (n - 3)S$$

For each mole of polythionate are formed two moles of thiosulfate which can be titrated iodometrically. With an excess of sulfide, the higher polythionates react very rapidly at room temperature, whereas trithionate reacts but slowly. However, at temperatures near the boiling point, even trithionate reacts quantitatively in a few minutes. In order to titrate the thiosulfate iodometrically, it is necessary first to remove the excess sulfide used; this is effected by precipitation as cadmium or zinc sulfide.

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[216] O. Schmitt, unpublished investigations.

[217] Cf. G. Chancel and E. Diacon, *Compt. rend.*, **56**, 710 (1863); W. Spring, *Ber.*, **7**, 1160 (1874); W. Feld, *Z. angew. Chem.*, **24**, 290, 1161 (1911); A. Sander, *Chem. Ztg.*, **41**, 657 (1917).

Schmitt[216] showed that the method suggested by Kurtenacker and Goldbach may yield slightly high values. He found that 20 ml. of zinc carbonate suspension is insufficient for the complete precipitation of 20 ml. of 0.4*N* sodium sulfide. The following amounts of zinc carbonate suspension were added to 20 ml. portions of 0.4*N* sodium sulfide solution which were then diluted to 250 ml. and filtered through dry filter paper. Then 100 ml. portions of filtrate were titrated with 0.1*N* iodine solution with the following results:

ml. $ZnCO_3$ suspension added	20	25	30	40
ml. 0.1*N* iodine used	7.82	0.58	0.37	0.22

On the basis of further studies, it was established that:

(*a*) if 40 ml. of zinc carbonate suspension is used and the solution diluted to 200 ml., a significant volume error is introduced by the zinc sulfide and zinc carbonate precipitates;

(*b*) an oxygen-free atmosphere should be used throughout the determination to avoid the oxidation of sodium sulfide;

(*c*) especially in the presence of trithionate, the sulfide solution should contain some polysulfide. Trithionate reacts with sulfide in two steps:[218]

$$S_3O_6^{2-} + S^{2-} \longrightarrow S_2O_3^{2-} + SO_3^{2-} + S$$

$$SO_3^{2-} + S \longrightarrow S_2O_3^{2-}$$

If the second step does not proceed to completion, excess iodine is required since sulfite is titrated rather than thiosulfate.

Procedure:

A. Bisulfite and Thiosulfate

1. Run an aliquot of the sample solution into an excess of acidified standard iodine solution and back-titrate the excess iodine with standard thiosulfate (*a* ml. of 0.1*N* iodine consumed).

2. To a second aliquot of sample solution add 5 ml. of approximately 40 per cent formaldehyde solution. If the solution is acid, add dilute sodium hydroxide to make the solution just alkaline to phenolphthalein. Allow to stand a few minutes, acidify with 20 ml. of 10 per cent acetic acid solution,

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[218] Cf. F. Raschig, *Z. angew. Chem.*, 33, 260 (1920); C. J. Hansen, *Ber.*, 66, 817 (1933).

and titrate with standard iodine solution to the starch end-point (*b* ml. of 0.1*N* iodine used).

B. Tetrathionate and Pentathionate

3. To a third aliquot of sample solution add approximately 30 ml. of 0.4*N* sodium sulfite solution and neutralize to phenolphthalein if necessary.[219] Allow the solution to stand for 5 minutes, then add 5 ml. of 40 per cent formaldehyde solution and 20 ml. of 10 per cent acetic acid, and titrate with standard iodine solution (*c* ml. of 0.1*N* iodine used).

4. Titrate a fourth portion of sample solution with iodine. Then dilute to 200–250 ml. with water, treat with 7 ml. of 10 per cent potassium cyanide solution, and neutralize if necessary.[219] After 5 minutes add 5 ml. of 40 per cent formaldehyde, acidify with 5 ml. of 1:4 sulfuric acid, and titrate with standard iodine solution until the starch-iodine color remains for at least 5 minutes (*d* ml. of 0.1*N* iodine used).

C. Trithionate

5. Titrate a fifth aliquot of sample solution with iodine solution in a 250 ml. Erlenmeyer flask. Then add to the solution 20 ml. of 0.4*N* sodium sulfide solution[220] and neutralize, if necessary, with alkali solution. Heat the solution as quickly as possible to the boiling point and keep near boiling for 10 minutes. Cool to room temperature, and add dropwise with vigorous shaking 40 ml. of freshly prepared zinc carbonate suspension.[221] Shake and allow the solution to stand until the supernatant liquid is clear. Filter the solution and wash the precipitate on a sintered-glass filter. Acidify the filtrate or an aliquot with 20 ml. of 10 per cent acetic acid and titrate with standard iodine solution. Run a blank titration on the reagents and calculate the net iodine consumed by the fifth aliquot of sample (*e* ml. of 0.1*N* iodine consumed).

Calculations: If equal volumes of sample solution are used in the individual titrations:

Millimoles of thiosulfate $= b/10$
Millimoles of sulfite $= (a - b)/20$
Millimoles of pentathionate $= (c - d - b/2)/10$
Millimoles of tetrathionate $= (2d - c)/10$
Millimoles of trithionate $= (e - 2d)/20$

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[219] In order to avoid the decomposition of polythionate on neutralization, add sulfite, cyanide, or sulfide to the acid solution; then add the required amount of alkali, as established by a preliminary test, for the exact neutralization.

[220] Dissolve 12 g. of $Na_2S \cdot 9H_2O$ in 20–25 ml. of water with very gentle heating. Add 0.2–0.3 g. of sulfur flowers and stir with a glass rod until completely dissolved. Filter the solution through a fluted filter into a 250 ml. volumetric flask and dilute to the volume mark with water.

[221] For preparation, see p. 295.

If the ratio of $c:d$ is between 3:1 and 2:1, hexathionate is present in the solution. Assuming the solution contains no tetrathionate, one calculates

$$\text{Millimoles of hexathionate} = (c - 2d)/10$$
$$\text{Millimoles of pentathionate} = (3d - c - b/2)/10$$

Notes: (1) For better results, Schmitt[216] recommends the use of an oxygen-free nitrogen atmosphere over the solution throughout the determination.

(2) Murthy[222] determines dithionate in the presence of sulfide, sulfite, thiosulfate, and other polythionates by oxidizing with alkaline permanganate, which destroys all these compounds except dithionate. The excess permanganate is removed by boiling with manganous sulfate, the solution is filtered, and the dithionate there is oxidized with standard dichromate in an acid medium. The excess of dichromate is determined iodometrically.

6. Hydrogen Cyanide. In neutral or weakly alkaline solution, cyanide reacts with iodine according to the equation:

$$CN^- + I_2 \rightleftharpoons ICN + I^-$$

or

$$HCN + I_2 \rightleftharpoons ICN + H^+ + I^-$$

According to Kovách,[223] the equilibrium constant for this reaction is

$$K = \frac{[I_2][HCN]}{[ICN][H^+][I^-]} = 1.37 \text{ at } 25^\circ \text{ C.}$$

Since the ionization constant of hydrocyanic acid is

$$K_{HCN} = \frac{[H^+][CN^-]}{[HCN]} = 7.2 \times 10^{-10}$$

it follows that

$$K' = \frac{[I_2][CN^-]}{[ICN][I^-]} = 9.9 \times 10^{-10}$$

It can be seen from these equilibrium constants that cyanide reacts quantitatively with iodine only in alkaline solution; it is also desirable to keep the concentration of iodide ion as low as possible.

Cyanide was titrated iodometrically by Fordos and Gélis[224] by titrating a very dilute, almost colorless solution with iodine solution to a persistent yellow color. Rupp[225] found it advantageous to carry out the titration in the presence of alkali bicarbonate, acetate, or Rochelle salt. In our experience, the end-point is more distinct in a carbonate-bicarbonate solution than in a bicarbonate solution. An acid solution is made alkaline with excess sodium hydroxide, and then sufficient sodium bicarbonate is added to give a carbonate-bicarbonate buffer. Borax may be used but the end-point is not so sharp as that in a carbonate-bicarbonate solution. Rupp found that starch cannot be used as indicator since iodine in iodine cyanide is held so loosely that the end-point appears too soon. In carbonate-bicarbonate medium, however, the correct end-point is observed with starch, but it is not advisable to use starch as indicator even in this medium, for the reaction between cyanide and iodine is measurably slow and the addition of starch makes it even slower. It is far better to use an organic solvent, such as benzene or carbon tetrachloride, which extracts iodine from aqueous solution, to detect the end-point. This is especially recommended for the iodometric titration of dilute cyanide solutions.

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[222] A. R. V. Murthy, *Current Sci.* (*India*), **22**, 371 (1953).

[223] L. Kovách, *Z. physik. Chem.*, **80**, 107 (1912).

[224] J. Fordos and A. Gélis, *J. pharm. chim.*, **23**, 48 (1853).

[225] E. Rupp, *Arch. Pharm.*, **241**, 328 (1903); **243**, 458 (1905); cf. S. J. M. Auld, *J. Chem. Soc.*, **93**, 1264 (1908).

Mercuric cyanide cannot be titrated by this method because of the very poor end-point. The modification of Rupp[226] in which the mercuric cyanide solution is added to iodine solution is no better.

Schulek[227] developed a very useful method which depends on the quantitative reaction of bromine with weakly alkaline solutions of cyanide (and also thiocyanate) to form bromine cyanide:

$$HCN + Br_2 \longrightarrow BrCN + H^+ + Br^-$$

Bromine cyanide is stable in weakly acid solution and does not react with phenol, hydrazine, ferrous, etc., even after 3 to 4 hours standing. Excess bromine may then be removed with these reagents and the bromine cyanide determined by reaction with iodide:

$$BrCN + 2I^- \longrightarrow CN^- + I_2 + Br^-$$

and titration of the liberated iodine with thiosulfate.

Procedure: Add to an iodine flask 50 ml. of sample solution containing 0.1–40 mg. of hydrocyanic acid (or 0.3–90 mg. of thiocyanic acid). Acidify the solution with 5 ml. of 20 per cent phosphoric acid and treat with bromine water to a persistent deep yellow color. Shake to mix the solution and allow the flask to stand for a few minutes. Add 2 ml. of 5 per cent phenol solution to remove excess bromine and shake repeatedly and thoroughly until all the bromine color disappears. Add 0.5 g. of potassium iodide. Mix thoroughly and allow to stand for a few minutes; titrate the solution with standard $0.01N$ or $0.1N$ thiosulfate solution, using starch as indicator.

Notes: (1) The titration should be carried out to a permanent end-point; the blue starch-iodine color should not return for 5–10 minutes.

(2) Chlorides, bromides, sulfides, sulfites, and thiosulfates do not interfere in

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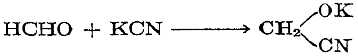
[226] E. Rupp, *Arch. Pharm.*, 241, 328 (1903).

[227] E. Schulek, *Z. anal. Chem.*, 62, 337 (1923).

this method. To separate cyanide from thiocyanate, the hydrocyanic acid is distilled from a solution containing much boric acid. Lang[228] ties up cyanide with formaldehyde in solutions acidified with acetic acid and determines the thiocyanate by the bromine cyanide method. Another procedure for the determination of hydrocyanic and thiocyanic acids is described by Lang;[229] iodate is used as the titrant.

(3) For the determination of hydrocyanic acid in coke-oven gas, Shaw *et al.*[230] absorb the gas in potassium hydroxide solution and add ammonium polysulfide solution to convert the cyanide to thiocyanate (thus avoiding the loss of cyanide when the solution is acidified). The solution is acidified with hydrochloric acid at room temperature, and carbon dioxide and other gases are evolved by evacuation without appreciable loss of thiocyanate. The thiocyanate is then converted to bromine cyanide with a potassium bromate-bromide solution, excess bromine removed with phenol, and bromine cyanide reduced with potassium iodide. After a 2 minute standing period, the vacuum is released and the iodine is titrated with thiosulfate.

Formaldehyde: In neutral or weakly alkaline solution, formaldehyde reacts with potassium cyanide:



$$HCHO + KCN \longrightarrow CH_2\begin{matrix}\nearrow OK \\ \searrow CN\end{matrix}$$

Romijn[231] introduced a method for the determination of formaldehyde in which a slight excess of potassium cyanide is added to the formaldehyde solution and the excess cyanide is determined by the Volhard method (cf. Vol. II, p. 266). Schulek[232] developed a simple method in which the excess cyanide is determined by the bromine cyanide method. This was modified by Mutschin.[233] In the presence of acetone, acetaldehyde, benzaldehyde, etc., the method yields better results than the acidimetric and direct iodometric procedures.

Procedure: Add the formaldehyde solution to an excess (approximately 50 per cent) of cyanide in an Erlenmeyer flask. Acidify the solution with concentrated hydrochloric acid (fume-cupboard!) and treat with bromine water until a clear yellow solution persists. Destroy the excess bromine by adding $0.025M$ hydrazine sulfate solution until the solution becomes colorless and then add 1–2 ml. in excess. Add a gram of potassium iodide and titrate the solution with standard $0.1N$ thiosulfate solution, using starch indicator.

Note: Schulek and Gervay[234] use the bromine cyanide procedure for the determination of hexamethylenetetramine (Urotropin) in the presence of various organic materials. Hexamethylenetetramine is split into formaldehyde and ammonia when heated with acid:

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[228] R. Lang, *Z. anal. Chem.*, **67**, 1 (1925).

[229] R. Lang, *Z. anorg. u. allgem. Chem.*, **142**, 280 (1925).

[230] J. A. Shaw, R. H. Hartigan, and A. M. Coleman, *Ind. Eng. Chem., Anal. Ed.*, **16**, 550 (1944).

[231] G. Romijn, *Z. anal. Chem.*, **36**, 18 (1897).

[232] E. Schulek, *Ber.*, **58B**, 732 (1925).

[233] A. Mutschin, *Z. anal. Chem.*, **99**, 335 (1934).

[234] E. Schulek and W. Gervay, *Z. anal. Chem.*, **92**, 406 (1933); *Magyar Gyógyszerésztud. Társaság Értesitöje*, **9**, 26 (1933), through *Chem. Abstr.*, **27**, 1984 (1933).

$$(CH_2)_6N_4 + 6H_2O + 4H^+ \longrightarrow 6HCHO + 4NH_4^+$$

The solution is neutralized and treated with an excess of potassium cyanide solution. Then the excess cyanide is determined by the procedure above. The titer of the cyanide solution is also determined by the bromine cyanide method. The cyanide consumed corresponds to the amount of hexamethylenetetramine. Each milliliter of $0.01N$ thiosulfate corresponds to 0.1168 mg. of $(CH_2)_6N_4$.

Salicylic acid and large amounts of piperazine, phenylsalicylic acid, phenylcinchoninic acid, and phenyl benzoate interfere. When these materials are present, Schulek and Gervay overcome the interference by distilling off the formaldehyde in the apparatus used for the determination of boric acid[235] and nitroglycerin.[236]

Silver: Schulek[237] found that a solution of potassium dicyanoargentate does not react appreciably with formaldehyde in 5 minutes, whereas free cyanide is completely removed. This is used as the basis for an iodometric method for the determination of silver. A neutral silver solution is treated with excess cyanide and the latter removed with formaldehyde. The solution is then acidified and treated with bromine water:

$$Ag(CN)_2^- + H^+ \longrightarrow AgCN + HCN$$

$$AgCN + HCN + 2Br_2 \longrightarrow AgBr + HBr + 2BrCN$$

After excess bromine is removed, the bromine cyanide is determined iodometrically.

Procedure: To a 125 ml. glass-stoppered flask add a measured amount of neutral silver solution containing 0.25–5 mg. of silver and dilute to about 30 ml. with water. Add from a dropping bottle 2 per cent potassium cyanide solution until the precipitate which forms at first redissolves. (If very little silver is present, no precipitate forms and 1–2 drops of cyanide solution suffice.) To remove the excess cyanide, add 1 or 2 drops of neutral 5 per cent formaldehyde solution and allow to stand for 5 minutes. Acidify the solution with 5 ml. of 20 per cent phosphoric acid and add saturated bromine water until a permanent yellow color is obtained. After 10 minutes add 2 ml. of 5 per cent phenol solution and allow to stand 2 minutes. Add 0.5 g. of potassium iodide with shaking. Stopper the flask, allow to stand in the dark for 10 minutes, and titrate with standard $0.01N$ thiosulfate solution, using starch as indicator. Each milliliter of $0.01N$ thiosulfate corresponds to 0.270 mg. of silver.

Notes: (1) Chloride and bromide do not interfere; the method can be applied to the determination of silver chloride precipitates.

(2) Acid solutions of silver are best neutralized to thymolphthalein.

(3) Schulek recommends the procedure for the determination of silver in organic preparations after destroying the organic materials.

7. Thiocyanate. Rupp and Schied[238] determine thiocyanate by oxidation in bicarbonate solution with excess standard iodine solution.

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[235] E. Schulek and G. Vastagh, *Z. anal. Chem.*, **84**, 167 (1931); **87**, 165 (1932).

[236] E. Schulek and B. Kerenyi, *Pharm. Zentralhalle*, **73**, 673, 692 (1932).

[237] E. Schulek, *Mikrochemie, Emich Festschrift*, **1930**, 260.

[238] E. Rupp and A. Schied, *Ber.*, **35**, 2191 (1902); *Arch. Pharm.*, **243**, 460 (1907).

$$SCN^- + 4I_2 + 4H_2O \longrightarrow SO_4^{2-} + 7I^- + ICN + 8H^+$$

The excess iodine is back-titrated with thiosulfate solution without reducing iodine cyanide. Since starch is affected by iodine cyanide, the disappearance of the yellow color of iodine is used to detect the end-point. Thiel[239] acidified the solution before back-titrating so that iodine cyanide was reduced. Schwicker[240] found an ammonium borate buffer more suitable than a bicarbonate solution for the oxidation of thiocyanate.

N Ammonium Borate Solution: Dissolve 20 g. of crystalline boric acid in 170 ml. of 10 per cent ammonia and dilute to 1 liter with water.

Procedure: Add a measured amount of thiocyanate solution to an excess of standard 0.1*N* iodine solution. Make the solution alkaline with 5–10 ml. of *N* ammonium borate solution. After 1–2 minutes, acidify the solution with 10 ml. of 2*N* sulfuric or hydrochloric acid and back-titrate the excess iodine with standard 0.1*N* thiosulfate solution.

The results are calculated on the basis of the equation

$$SCN^- + 3I_2 + 4H_2O \longrightarrow SO_4^{2-} + HCN + 7H^+ + 6I^-$$

since the iodine cyanide formed in weakly alkaline medium is reduced in acid solution.

Notes: (1) Pagel and coworkers[241] obtained good results if at least 5 ml. of 0.1*N* iodine solution in excess was used for the oxidation of thiocyanate. They also found that borax or an ammonia-ammonium salt buffer might be used to replace the ammonium borate when enough was added to keep the solution well buffered and when the solution was allowed to stand at least 5–10 minutes before acidification and back-titration.

Procedure: To the thiocyanate solution add 5 g. of borax and dilute with water to *ca.* 150 ml. Add standard 0.1*N* iodine solution until the excess iodine color disappears only slowly, then add 10 ml. more. (After 5 minutes compare the color of the solution with 150 ml. of water containing 5 ml. of 0.1*N* iodine solution to make sure that at least 5 ml. of iodine solution in excess is used.) After 10 minutes acidify the solution with 10 ml. of 6*N* hydrochloric acid and titrate at once with standard 0.1*N* thiosulfate solution.

(2) Angelescu and Popescu[242] investigated the kinetics of the iodometric oxidation of thiocyanate in weakly and strongly alkaline solutions. In bicarbonate solution, the rate-determining reaction is represented by the equation

$$SCN^- + IO^- \longrightarrow ICN + SO^{2-}$$

where SO^{2-} is a free radical which reacts very quickly with iodine:

$$SO^{2-} + 3I_2^- + 3H_2O \longrightarrow SO_4^{2-} + 6I^- + 6H^+$$

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[239] A. Thiel, *Ber.*, **35**, 2766 (1902).

[240] A. Schwicker, *Z. anal. Chem.*, **77**, 278 (1929).

[241] H. A. Pagel and O. C. Ames, *J. Am. Chem. Soc.*, **52**, 2698 (1930); H. A. Pagel and H. J. Koch, *ibid.*, **53**, 1774 (1931).

[242] E. Angelescu and V D. Popescu, *Z. physik. Chem.*, **156**, 258 (1931)

In the presence of sodium hydroxide the mechanism is the same up to the formation of iodine cyanide, but the rate-determining reaction is different. Iodine cyanide is stable in the presence of bicarbonate but is hydrolyzed slowly in the presence of sodium hydroxide. In sodium hydroxide solution the rate-determining reaction is

$$ICN + 2OH^{+} \longrightarrow CNO^{-} + I^{-} + H_2O$$

If ammonia or ammonium borate is used as the alkali, the oxidation is practically instantaneous since the concentration of hypoiodite is increased and iodine cyanide is not hydrolyzed.

The bromine cyanide procedure of Schulek (cf. under cyanide, p. 303) is probably the best iodometric method for the determination of thiocyanate and is strongly recommended. It is simple to carry out and yields accurate results. Reducing agents, such as sulfite, sulfide, thiosulfate, and bromide, do not interfere. If cyanide is present in the solution, it may be removed, e.g., by volatilization, or rendered harmless before the determination of thiocyanate.

Zinc: Spacu and coworkers[243] showed that zinc is precipitated quantitatively by pyridine and thiocyanate as white crystals of $Zn(Py)_2(SCN)_2$. Pagel and Ames[244] utilized this observation for the volumetric determination of zinc. Since pyridine interferes with the iodometric determination of thiocyanate, the precipitate is first boiled with borax solution to remove pyridine.

Procedure: Dissolve 1 g. of potassium thiocyanate in 100 ml. of solution containing 3–33 mg. of zinc. Add dropwise, while stirring the solution, 1 g. of pyridine. Keep the mixture below 20° for an hour, shaking now and then to precipitate the zinc quantitatively. Separate the precipitate on a Gooch crucible fitted with a snug filter paper disk, and wash with a 1 per cent potassium thiocyanate–1 per cent pyridine solution. Finally, wash the precipitate with not more than 10 ml. of water-free ether containing 1 per cent pyridine (cooled to 20° or lower) and suck free of solvent. Invert the crucible over a 500 ml. wide-mouth Erlenmeyer flask and dislodge the filter paper and precipitate; wash out the crucible with hot water and bring the volume of solution to *ca.* 150 ml. Heat the solution to dissolve the precipitate and add 6 g. of borax. Continue heating for 10 minutes to volatilize the pyridine. Cool the solution, add a slight excess of standard iodine solution, and continue as in the simple thiocyanate determination.

Note: In the presence of halides and ammonium salts, low results are obtained. Sulfate and nitrate do not interfere. Magnesium and the alkaline earth metals do not interfere, but copper, cadmium, cobalt, nickel, and manganese form slightly soluble pyridine thiocyanates and thus interfere.

Polysulfide: Schulek[245] applied the determination of thiocyanate to the determination of polysulfide. Alkali metal cyanides react with soluble polysulfides to form a thiocyanate ion for each polysulfide sulfur. If this reaction is carried out in a boric acid solution, hydrogen sulfide and hydrogen cyanide may be distilled off while the thiocyanate and any thiosulfate present in the sample remain unaffected. The thiocyanate may be determined in the presence of thiosulfate by acidifying the solution and using the bromine cyanide method.

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[243] G. Spacu and R. Ripan, *Z. anal. Chem.*, 64, 338 (1924); G. Spacu and J. Dick, *ibid.*, **73**, 356 (1928).

[244] H. A. Pagel and O. C. Ames, *J. Am. Chem. Soc.*, 52, 3093 (1930).

[245] E. Schulek, *Z. anal. Chem.*, 65, 352 (1925).

Procedure: Dissolve 1 g. of boric acid in 50–60 ml. of water in a 125 ml. round-bottom flask. Boil the solution for 1–2 minutes to expel air from the flask. Keeping the solution hot, add 0.5–2 ml. of 10 per cent potassium cyanide, depending on the amount of polysulfide sulfur to be determined. Now add a measured amount of polysulfide solution which should not contain more than 0.2 g. of polysulfide sulfur. Boil the solution briskly for 10 minutes. The pH of the solution should be below 7 to ensure the complete evolution of hydrogen cyanide. If the sample is very alkaline, use more boric acid to obtain the necessary acidity. Cool the solution, transfer quantitatively to a glass-stoppered flask, and acidify with 1–2 ml. of concentrated hydrochloric acid. Add bromine water dropwise until a permanent yellow color persists. Add 5–10 ml. of 3 per cent phenol solution and allow to stand for 10 minutes to remove excess bromine. Add 0.5–1 g. of potassium iodide, allow the solution to stand for a few minutes, and titrate with standard thiosulfate solution. Each milliliter of $0.1N$ thiosulfate corresponds to 1.603 mg. of polysulfide sulfur.

Note: The solution obtained after boiling with cyanide and cooling may be transferred quantitatively to a volumetric flask and diluted to a known volume. The polysulfide sulfur, which is present as thiocyanate, is determined as outlined above in an aliquot portion of this solution. The thiosulfate sulfur may then be determined in a second aliquot portion of the solution by acidifying with 10 ml. of N hydrochloric acid, treating with an excess of standard $0.1N$ or $0.01N$ iodine solution, and back-titrating with standard $0.1N$ or $0.01N$ thiosulfate solution. Each milliliter of $0.1N$ iodine solution corresponds to 6.40 mg. of thiosulfate sulfur.

8. Nitrogen Compounds. ***Hydrazine:*** The iodometric titration of hydrazine has been discussed briefly on p. 233. Curtius and Schulz[246] showed that a solution of hydrazine reacts with an alcoholic solution of iodine according to the equation

$$N_2H_4 + 2I_2 \longrightarrow N_2 + 4H^+ + 4I^-$$

The reaction is rapid in alkaline solution but slow in acid solution. On the basis of this reaction, Stollé[247] titrated hydrazine in a bicarbonate solution with iodine solution. Since the reaction is not instantaneous, the titration is carried out as slowly as possible toward the end until the iodine color persists for 2–4 minutes.

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[246] T. Curtius and H. Schulz, *J. prakt. Chem.*, (2) **42**, 539 (1890).

[247] R. Stollé, *J. prakt. Chem.*, [2] **66**, 332 (1902).

Kolthoff[248] tested the method and obtained good results. However, too much bicarbonate must be avoided, for low results are obtained at high pH values because of the decomposition of hydrazine. A suitable amount of sodium bicarbonate is 0.5–1 g. in 25 ml. of approximately $0.1N$ hydrazine solution. In the presence of starch, the reaction of hydrazine and iodine is very slow, especially near the end-point; thus it is preferable to use the yellow color of iodine, which persists for at least 2 minutes, to mark the end-point. In this way, the whole determination can be completed in less than 7 minutes.

Rupp[249] recommended the use of Rochelle salt or sodium acetate in place of bicarbonate, the addition of excess standard iodine solution, and back-titration of the excess with thiosulfate after 15 minutes. Kolthoff tested these buffers for the direct titration of hydrazine with iodine. Good results were obtained but, since the reaction of hydrazine and iodine is appreciably slower at the lower pH, an excessive amount of time was required for the titration.

In order to speed up the determination, Bray and Cuy[250] add an excess of iodine and sodium hydroxide to the hydrazine solution in a glass-stoppered flask. The alkali is added last since iodine and alkali react fairly rapidly to form iodate which can cause low results. On the other hand, hydrazine in the presence of alkali and air decomposes slowly to yield low results. After 2 minutes the solution is acidified and back-titrated with sodium thiosulfate solution. This method is rapid and exact. The amounts of reagents and reaction time are not critical. Good results were obtained with 3–50 per cent excess iodine and with final concentrations of alkali from 0.008 to $0.5N$. The reaction time was extended to 30 minutes with no adverse effects. Some prefer to oxidize hydrazine with iodate and to determine the excess iodometrically.[251] The titration of phenylhydrazine is based upon the reaction[252]

$$C_6H_5NHNH_2 + 2I_2 \longrightarrow N_2 + C_6H_5I + 3H^+ + 3I^-$$

The titration is carried out best by adding a solution of phenylhydrazine to an excess of standard iodine solution, which is then back-titrated with thiosulfate.

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[248] I. M. Kolthoff, *J. Am. Chem. Soc.*, **46**, 2009 (1924).

[249] E. Rupp, *J. prakt. Chem.*, [2] **67**, 140 (1903).

[250] W. C. Bray and E. J. Cuy, *J. Am. Chem. Soc.*, **46**, 858 (1924).

[251] E. Rimini, *Chem. Zentr.*, 1899, II, 455; 1906, II, 1662; cf. C. F. Hale and H. W. Redfield, *J. Am. Chem. Soc.*, **33**, 1353 (1911); A. W. Browne and F. F. Shetterley, *ibid.*, **30**, 59 (1908); W. C. Bray and E. J. Cuy, *ibid.*, **46**, 858 (1924).

[252] E. von Meyer, *J. prakt. Chem.*, (2) **36**, 115 (1887); P. Fromm, *Apoth. Ztg.*, **12**, 254 (1897); cf. P. Endröi, *Magyar Kem. Folyóirat*, **59**, 211 (1953).

Endröi[252] adds the sample to 20 ml. of water and 2 ml. of 10 per cent hydrochloric acid, dilutes to 100 ml., and titrates with $0.1N$ iodine. A further equivalent amount of iodine is added, followed by 20 ml. of saturated disodium hydrogen phosphate. After 5 minutes, 4 ml. of 10 per cent hydrochloric acid is added and the excess of iodine is titrated with thiosulfate.

Nitrous Acid and Its Salts. Nitrous acid is a weak acid whose ionization constant is given by the equation[253]

$$K = \frac{[H^+][NO_2^-]}{[HNO_2]} = 6.0 \times 10^{-4} \text{ at } 30° \text{ C.}$$

Thus, when a strong acid is added to a solution of nitrite, nitrous acid is formed, which in turn decomposes at a measurable rate according to the equation

$$3HNO_2 \rightleftharpoons H^+ + NO_3^- + 2NO + H_2O$$

The reaction is reversible and its mechanism has been studied thoroughly by Abel and coworkers.[254]

Nitrous acid reacts with iodide in acid solution according to the equation

$$2HNO_2 + 2I^- + 2H^+ \longrightarrow 2NO + I_2 + 2H_2O$$

The liberated iodine cannot be titrated directly since nitric oxide reacts with oxygen and liberates additional iodine. Iodine also reacts with nitrous acid according to the equation

$$HNO_2 + I_2 + H_2O \longrightarrow NO_3^- + 2I^- + 3H^+$$

but the reaction is very slow. The complex mechanism of this reaction has been studied by Durrant and coworkers.[255] Various authors[256] have investigated the removal of oxygen and the reliability of the nitrous acid-iodide reaction for the determination of nitrite. According to Davisson[257] these procedures are not accurate; but the procedure given by this author also gives variable results (between −1.5 and +2.5 per cent error). Dienert[258] gives an elaborate procedure which, however, is not more accurate than 2 per cent for 3 mg. of nitrite nitrogen. According to Abeledo and Kolthoff,[259] the following procedure gives reliable results.

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[253] A. Klemenc and E. Hayek, *Monatsh.*, **53–54**, 407 (1929).

[254] E. Abel and H. Schmid, *Z. physik. Chem.*, **132**, 55, 64 (1928); **134**, 279 (1928); **136**, 430 (1928); E. Abel, H. Schmid, and S. Babad, *ibid.*, **136**, 135, 419 (1928); E. Abel, H. Schmid, and J. Weiss, *ibid.*, **147**, 69 (1930); E. Abel, H. Schmid, and F. Römer, *ibid.*, **148**, 337 (1930); cf. W. C. Bray, *Chem. Revs.*, **10**, 161 (1932).

[255] G. G. Durrant, R. O. Griffith, and A. McKeown, *Trans. Faraday Soc.*, **32**, 999 (1936).

[256] L. W. Winkler, *Chem. Ztg.*, **23**, 454, 541 (1899); **25**, 586 (1901); *Z. Untersuch. Nahr. u. Genussm.*, **29**, 10 (1915); J. Meisenheimer and F. Hein, *Ber.*, **38**, 3834, 4136 (1905); F. Raschig, *ibid.*, **38**, 3911 (1905).

Procedure: To a 250 ml. glass-stoppered Erlenmeyer flask add 10–12 g. of sodium bicarbonate, 3 g. of potassium iodide, 0.5–1 ml. of amyl alcohol, and 25 ml. of water. Then add a measured amount of nitrite solution. Mix the contents of the flask by shaking. After most of the sodium bicarbonate settles, add about 4 ml. of acetic acid from a pipette in such a way that the acid is distributed through the solution without shaking. Loosely stopper the flask. After the evolution of carbon dioxide has nearly ceased, gently rotate the flask. After the sodium bicarbonate settles, add quickly, without shaking, 6–7 ml. of $20N$ sulfuric acid. Loosely stopper the flask and gently rotate to mix the solution when evolution of carbon dioxide nearly ceases. Rinse down the stopper and sides of the flask, and titrate the solution with standard thiosulfate solution, using starch as indicator. After the end-point is reached, stopper the flask and allow to stand for 10 minutes. If the solution requires more than 0.1–0.2 ml. of $0.1N$ thiosulfate to decolorize it, the procedure must be repeated.

Notes: (1) A large excess of bicarbonate is necessary in order to remove all nitric oxide as it is formed, with carbon dioxide. Sodium bicarbonate cannot be replaced by the more soluble potassium salt.

(2) Since oxygen interferes strongly in the reaction of iodide and nitrite, it must be removed before the addition of strong acid; this is accomplished with acetic acid. The hydrogen-ion concentration is sufficiently low that very little, if any, reaction between iodide and nitrite takes place when acetic acid is added.

(3) Amyl alcohol need not be used, but it is strongly recommended to prevent over-foaming of solution during the evolution of carbon dioxide.

(4) If air is not removed completely, iodine is formed after the end-point is reached. In order to test the reliability of the results, the solution is titrated after standing 10–15 minutes. If more than 0.2 ml. of $0.1N$ thiosulfate is required, the results are not reliable.

(5) Very dilute nitrite solutions (*ca.* $0.005N$) can be determined with an accuracy of about 0.5 per cent.

(6) Good results are obtained in the presence of 2–3 per cent ethanol and amyl alcohol. Therefore the procedure is suitable for the determination of nitrites in the presence of these materials (e.g., in amyl and ethyl nitrite) where the permanganate procedure fails.

(7) Rao and Pandalai[260] titrated very dilute (2×10^{-4} N) nitrite solution in

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[257] B. S. Davisson, *J. Am. Chem. Soc.*, **38**, 1683 (1916).

[258] F. Dienert, *Ann. chim. anal. et chim. appl.*, (2) **1**, 4 (1919).

[259] C. A. Abeledo and I. M. Kolthoff, *J. Am. Chem. Soc.*, **53**, 2893 (1931).

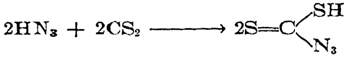
[260] G. G. Rao and K. M. Pandalai, *Analyst*, **59**, 99 (1934).

the following manner. Place 20 ml. of nitrite solution in a 250 ml. flask. Add about 4 g. of sodium bicarbonate, 5 ml. of 10 per cent potassium iodide solution, and starch indicator. Bubble pure carbon dioxide through the solution for 10 minutes to remove oxygen, and acidify with 10 ml. of $5N$ oxygen-free sulfuric acid. The nitric oxide formed is removed by the generated carbon dioxide, and the iodine is titrated with freshly prepared standard $2 \times 10^{-3}\,N$ thiosulfate solution. The average error of the method is given as 0.25 per cent.

Hydrazoic Acid and Azides: Hydrazoic acid is a weak acid whose ionization constant is[261]

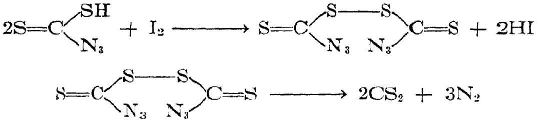
$$K_a = \frac{[H^+][N_3^-]}{[HN_3]} = 1.8 \times 10^{-5} \text{ at } 25°\text{C}.$$

Solutions of hydrazoic acid and azides behave as both oxidizing and reducing agents; however, in general, they are not very reactive at room temperature. Hydrazoic acid and iodine react only in the presence of a catalyst. Catalysts which have been used include thiosulfate and carbon disulfide. In the latter case azidodithiocarbonic acid is formed by the reaction of carbon disulfide with hydrazoic acid or azide solutions, which is accelerated by acetone or alcohol.[262]



$$2HN_3 + 2CS_2 \longrightarrow 2S{=}C\begin{matrix}\diagup SH \\ \diagdown N_3\end{matrix}$$

If the reaction takes place in the presence of excess iodine, the azidodithiocarbonic acid which forms is oxidized to nitrogen and carbon disulfide. According to Feigl and Chargaff,[263] this process may be represented by the equations



The overall reaction is thus given by the equation

$$2HN_3 + I_2 \longrightarrow 2HI + 3N_2$$

Procedure:[263] Add to a 500 ml. flask 0.5 ml. of carbon disulfide, 6–8 ml. of acetone, and a moderate excess of standard $0.1N$ iodine solution. Then add a measured amount of the test solution. When the solution is stirred, nitrogen gas is evolved. When the evolution of gas ceases (5–10 minutes), dilute the solution with 250 ml. of water and back-titrate the excess iodine with standard $0.1N$ arsenite [or thiosulfate—Authors] solution, using starch as indicator.

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[261] C. A. West, *J. Chem. Soc.*, **77**, 705 (1900).

[262] F. Sommer, *Ber.*, **48**, 1833 (1915); A. J. Currier and A. W. Browne, *J. Am. Chem. Soc.*, **44**, 2849 (1922).

[263] F. Feigl and E. Chargaff, *Z. anal. Chem.*, **74**, 376 (1928).

Note: Feigl and Chargaff recommend that the amount of iodine required be determined approximately in a preliminary titration so that 1–2 ml. of iodine solution in excess may be used in the exact determination.

Quaternary Ammonium Compounds. High molecular weight quaternary ammonium compounds in aqueous solution form slightly soluble triiodides when a solution containing iodine and potassium iodide is added:

$$\underset{\text{colorless}}{QN^+} + KI_3 \longrightarrow \underset{\text{yellow}}{QNI_3} + K^+$$

In the equation QN^+ represents a completely substituted quaternary ammonium ion and KI_3 is the active material in ordinary iodine-iodine solution. If an excess of iodine solution is added, quaternary ammonium polyiodides are formed:

$$\underset{\text{yellow}}{QNI_3} + KI_3 \longrightarrow \underset{\substack{\text{brownish}\\\text{orange}}}{QNI_x} + KI$$

On the other hand, if the quaternary ammonium triiodide is washed excessively with potassium iodide solution, iodine is lost:

$$\underset{\text{yellow}}{QNI_3} + KI \longrightarrow \underset{\text{white}}{QNI} + KI_3$$

Hager *et al.*[264] determined quaternary ammonium salts in textiles and paper by forming the triiodide *in situ*, rinsing with a potassium iodide solution to yield the fairly stable triiodide, extracting the triiodide in alcohol, diluting the solution with water, acidifying, and titrating with standard thiosulfate solution. Each mole of quaternary ammonium triiodide reacts with two equivalents of thiosulfate. Hager *et al.* also describe a more versatile and precise method of analysis which involves the direct titration of quaternary ammonium salt solution with standard iodine solution using a potentiometric end-point. The original article should be consulted for further details.

9. Arsenic. ***Trivalent Arsenic:*** The iodometric titration of arsenic trioxide has been discussed on pp. 217–218 and 231. It is generally advantageous to carry out the titration in a bicarbonate solution in which the reaction with iodine proceeds very smoothly and quantitatively.

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[264] O. B. Hager, E. M. Young, T. L. Flanagan, and H. B. Walker, *Anal. Chem.* 19, 885 (1947).

Arsenic in Organic Compounds: The titration of trivalent arsenic in organic compounds is generally carried out readily. Dehn[265] describes the oxidation of methylarsine with iodine:

$$CH_3AsH_2 + 3I_2 + 3H_2O \longrightarrow CH_3AsO(OH)_2 + 6HI$$

Bougault[266] describes the oxidation of methyldiiodoarsine and methylarsine oxide:

$$CH_3AsI_2 + I_2 + 3H_2O \longrightarrow CH_3AsO(OH)_2 + 4HI$$

$$CH_3AsO + I_2 + 2H_2O \longrightarrow CH_3AsO(OH)_2 + 2HI$$

These reactions take place very quickly in acid solution. Fleury[267] investigated the oxidation of arsenious oxide and its phenyl derivatives. The equilibrium of the reaction, the reaction velocity, the influence of solvents, and the effect of iodides were studied. With the introduction of phenyl groups to the arsenious oxide, the reaction remains the same but the reactivity increases:

$$R_3As + I_2 \rightleftharpoons R_3AsI_2$$

$$R_3AsI_2 + H_2O \rightleftharpoons R_3AsO + 2HI$$

where R is a phenyl or hydroxyl group. For quantitative determinations, the titration is carried out in the presence of bicarbonate in alcohol-water solution or, in the case of triphenylarsine, in chloroform or benzene solution. The procedure is useful for the analysis of mixtures of arsenic trichloride, phenyldichloroarsine, diphenylchloroarsine and triphenylarsine.

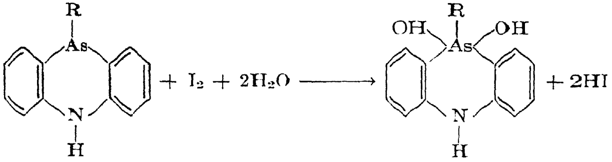
According to Frahm and Boogaert,[268] diphenylchloroarsine and diphenylarsine oxide react quantitatively with iodine in the presence of sodium bicarbonate:

$$Ph_2AsCl + I_2 + 2H_2O \longrightarrow Ph_2AsO(OH) + 2HI + HCl$$

$$Ph_2AsO + {}^1/_2I_2 + H_2O \longrightarrow Ph_2AsO(OH) + HI$$

These substances are dissolved in benzene, treated with a 4 per cent aqueous solution of sodium bicarbonate, and titrated with iodine solution until the benzene phase shows the presence of iodine after vigorous shaking in a glass-stoppered flask.

Rasuwajew and Malinowski[269] titrated the alkyl and aryl derivatives of 9,10-dihydrophenarsazine, 10-chloro-9,10-dihydroxyphenarsazine, 9,10-dihydrophenarsazine oxide, and phenoxarsine oxide with an alcoholic solution of iodine. The oxidation of the alkyl and aryl derivatives proceeds according to the equation



The oxidation of the chloro derivative and the oxides in alcohol-water solution with alcoholic iodine solution results in the formation of the corresponding phenarsazinic and phenoxarsinic acids. The oxidation of phenarsazine and phenarsazine oxide is better in the presence than in the absence of bicarbonate, but the alkyl and aryl derivatives react easily in its absence.

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[265] W. M. Dehn, *Am. Chem. J.*, **33**, 101 (1905).

[266] J. Bougault, *J. pharm. chim.*, (6) **26**, 193 (1907).

[267] P. Fleury, *Bull. soc. chim. France*, (4) **27**, 490, 699 (1920).

[268] E. D. G. Frahm and H. L. Boogaert, *Rec. trav. chim.*, **49**, 623 (1930).

[269] G. A. Rasuwajew and W. S. Malinowski, *Ber.*, **64B**, 120 (1931).

Procedure According to Rasuwajew and Malinowski:[269] .The sample is dissolved in 15–20 ml. of alcohol, diluted with water until the solution becomes cloudy, and titrated with an alcoholic solution of iodine until a bright yellow color appears. In the course of the titration, water is added 2–3 times so that the total volume of solution is 60–100 ml. The color appearing on the addition of the first portions of iodine disappears quickly on shaking. Toward the end of the titration 10–30 seconds is required for the disappearance of the color. Finally, the addition of 1–2 drops of iodine solution in excess produces a bright yellow color which persists for 24–48 hours.

Note: Since a pure alcoholic solution of iodine is not stable it is recommended that some iodide be added. Such a solution is stable for a longer time.

Arsenic after Reduction to the Element. Hypophosphorous acid in strongly acid solution reduces tri- and pentavalent arsenic to the element when heated.[270] Brandt[271] makes this reaction the basis for a simple iodometric method for determining arsenic which is useful for trace amounts. Evans[272] developed the method for determining arsenic in alloys and steel.

Procedure: Treat the arsenic-containing solution with at least an equal volume of concentrated hydrochloric acid and then with 3–5 g. of sodium hypophosphite. Warm the solution gently (keep the temperature below 50 °) to reduce copper, iron. etc., then add 10 g. of sodium hypophosphite and boil for 15 minutes under a reflux condenser. Arsenic precipitates as a dark brown powder. Cool the solution and filter through filter paper pulp previously treated with bromine and hydrochloric acid and washed with water. Wash the precipitate with 1:3 hydrochloric acid containing about 2 per cent sodium hypophosphite and then 6 or 7 times with 5 per cent ammonium chloride solution. Transfer the filter to a flask, rinse with water, add 2 g. of sodium bicarbonate and a measured excess of standard iodine solution, stopper the flask, shake to mix the solution thoroughly, and allow to stand for 5 minutes. Dilute the solution to about 300 ml. with water, add 2 g. of sodium bicarbonate, and back-titrate the iodine with standard arsenite solution. If the endpoint is not sharp add a slight excess of arsenite and back-titrate with standard iodine solution.

The equivalent weight of arsenic is 14.98.

Notes: (1) Very small amounts of arsenic (e.g., 0.01 mg.) may be titrated satisfactorily by this method. Naturally, arsenic-free reagents must be used and a blank correction made.

(2) Oxidizing substances must be made harmless. Nitric acid may be fumed off with sulfuric acid or reduced with sodium hypophosphite. Cupric ion is reduced to cuprous in the presence of sufficient hydrochloric acid. Ferric ion is only very slowly reduced by hypophosphite; this reduction is accelerated by cop-

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[270] J. Thiele, *Ann.*, **263**, 361 (1890); *Apoth. Ztg.*, **5**, 86 (1890).

[271] L. Brandt, *Chem. Ztg.*, **37**, 1445, 1471, 1496 (1913); **38**, 295, 461, 474 (1914).

[272] B. S. Evans, *Analyst*, **52**, 565 (1927); **54**, 523 (1929); **57**, 492 (1932); cf. J. Haslam and N. T. Wilkinson, *ibid.*, **78**, 390 (1953).

per. If appreciable amounts of these oxidants are present, correspondingly larger amounts of sodium hypophosphite must be used than prescribed above.

(3) For the determination of arsenic in copper, bronze, steel, and alloys, consult the original article by Evans.[272]

(4) Andrews and Farr[273] used stannous chloride to reduce arsenic to the metal, which is then determined iodometrically. Shatko[274] reduced with a chromous solution.

Pentavalent Arsenic: As discussed already (p. 217), the reaction

$$H_3AsO_3 + I_3^- + H_2O \rightleftharpoons H_3AsO_4 + 2H^+ + 3I^-$$

is reversible and the equilibrium constant of the reaction is 0.16.

According to Rosenthaler,[275] the reaction is quantitative within 10–15 minutes in the presence of much acid. The hydrochloric acid concentration should be at least 12–16 per cent; heating is unnecessary.

Kolthoff[276] investigated the reaction systematically and always obtained good results if the hydrochloric acid concentration in the final titration mixture was at least 4*N*, if the reaction mixture was allowed to stand at least 5 minutes before the liberated iodine was titrated, and if the titration was carried out at room temperature with constant stirring to prevent the decomposition of thiosulfate in the strongly acid solution. In 3*N* hydrochloric acid, the results obtained were about 1 per cent low. The same error obtains if the solution is diluted with water before being titrated since part of the arsenious acid is oxidized to arsenic acid by the iodine at the lower acidity. Time has no influence so long as 5 minutes of standing is allowed before titration. Increasing temperature causes low results; at 50°C. results were 16 per cent low.

Procedure: To 10 ml. of approximately 0.2*N* arsenate solution in an iodine flask add 20 ml. of 25 per cent hydrochloric acid. Free the solution of air by adding some sodium bicarbonate. Treat with 1 g. of potassium iodide, stopper the flask, mix, allow to stand for at least 5 minutes, and titrate the solution with standard 0.1*N* thiosulfate solution, agitating thoroughly.

Note: In the titration of 0.02*N* arsenate, the hydrochloric acid concentration should be at least 4.5*N*. Catalytic agents such as molybdate, tungstate, vanadate, ferrous, manganous, uranyl, and chromic ions have no effect on this method.

Because of the difficulties they encountered in the titration of strongly acid iodine solution with thiosulfate, Gooch *et al.*[277] reduced arsenate by heating with potassium iodide and sulfuric acid; most of the liberated iodine was removed by boiling, the last traces of iodine were reduced by careful addition of sulfurous acid, and the solution was diluted and neutralized with potassium carbonate and bicarbonate; finally the arsenite was titrated with standard iodine solution, starch being used as indicator. This procedure is tedious and involves the danger of forming volatile arsenic triiodide during the evaporation.

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[273] L. W. Andrews and H. V. Farr, *Am. J. Sci.*, 27, 316 (1909); *Z. anorg. Chem.*, 62, 123 (1909).

[274] P. P. Shatko, *Zhur. Anal. Khim.*, 7, 242 (1952).

[275] L. Rosenthaler, *Z. anal. Chem.*, 45, 596 (1906).

[276] I. M. Kolthoff, *Pharm. Weekblad*, 56, 1322 (1919); 58, 727 (1921).

Fleury[278] critically reviewed the above methods and suggested the following modified method.

Procedure: Dissolve the arsenate (equivalent to approximately 50 ml. of $0.1N$ iodine) in 30 ml. of water. Make the solution about $1N$ in hydrochloric acid, heat on a water bath for 5 minutes, add potassium iodide to make its concentration 25 per cent, and heat for 5–10 minutes longer on the water bath. No free iodine is lost in this process. Cool and titrate (or exactly reduce) the liberated iodine with sodium thiosulfate. Arsenic is now all in the trivalent state. Treat the solution copiously with sodium bicarbonate and titrate the trivalent arsenic with standard $0.1N$ iodine solution.

Kolthoff found that the liberated iodine may be titrated directly in the following way:

Procedure: To 10 ml. of arsenate solution in an iodine flask add 2.5 ml. of $4N$ hydrochloric acid. Heat the mixture on a boiling water bath for 3 minutes, add 3 g. of potassium iodide, and immediately stopper the flask. Heat on the water bath for 5–10 minutes longer, cool the solution rapidly, and titrate the free iodine with standard thiosulfate solution. As a check, an excess of bicarbonate may be added to this solution and the arsenite then titrated with standard iodine solution.

Notes: (1) Since air is expelled in the initial heating of the solution there should be no fear of air-oxidation of iodide in the acid solution.

(2) Shakhtakhtinskiĭ[279] removes the liberated iodine with an organic solvent. He recommends an acidity of $5N$ in hydrochloric acid or $8N$ in sulfuric acid for the reduction and dilution to $3N$ or $4N$, respectively, before titration with thiosulfate. Twice the theoretical amount of potassium iodide and 20 ml. of chloroform or benzene should be added. After shaking for a few seconds the iodine is titrated with standard thiosulfate.

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[277] F. A. Gooch and P. E. Browning, *Am. J. Sci.*, **40**, 66 (1891); F. A. Gooch and J. C. Morris, *ibid.*, **10**, 151 (1900).

[278] P. Fleury, *J. pharm. chim.*, **21**, 385 (1920).

[279] G. B. Shakhtakhtinskiĭ, *Zhur. Anal. Khim.*, **9**, 233 (1954).

Kurtenacker and Fürstenau[280] reduce arsenate with sulfurous acid. The reaction is slow but is accelerated greatly by small amounts of hydrochloric or sulfuric acid; the maximum speed is attained when the acids are $0.13M$. The excess sulfurous acid is removed, the solution neutralized, and the arsenite titrated with iodine solution.

Procedure: To the arsenate solution in an iodine flask add 4 to 5 g. of anhydrous sodium sulfite. Dilute the solution to 50 ml. with water and add 5–6 ml. of 1:1 sulfuric acid. Stopper the flask and warm in a hot water bath for 20–25 minutes. Remove the stopper and boil the solution over an open flame for 5 minutes to remove most of the excess sulfur dioxide. Cool the solution and neutralize with sodium hydroxide solution to the phenolphthalein end-point. Add 5 ml. of formaldehyde to tie up the remaining sulfite, add 20 ml. of 10 per cent acetic acid and 10 ml. of 40 per cent sodium acetate solution, and titrate the solution with standard $0.1N$ iodine solution. Since the reaction is very slow near the end-point, it is better to add a small excess of standard iodine solution and back-titrate with standard thiosulfate solution.

Notes: (1) Tribalat[281] reduces arsenate with stannous chloride in a sulfuric–tartaric acid solution with potassium perrhenate as catalyst. The excess stannous in the acid solution (around pH 0) is oxidized with iodine solution until the blue starch-iodine color just appears. The solution is then neutralized and diluted (pH around 8.3) and the trivalent arsenic titrated with iodine solution.

(2) FitzGibbon[282] uses very finely divided (passed through 100 mesh sieve) amorphous phosphorus in the presence of iodide and sulfuric acid to reduce arsenate to arsenite. The mixture is boiled to effect reduction, the phosphorus is filtered off and the solution neutralized and titrated with iodine solution.

(3) The iodometric titration of arsenate may be used for the determination of cations which form slightly soluble arsenates of constant composition. This application of the arsenate titration has been suggested especially for the determination of magnesium.[283]

10. Antimony. ***Trivalent Antimony:*** The titration of trivalent antimony with iodine in concentrated bicarbonate solution is carried out like that of trivalent arsenic. The antimony is kept in solution with tartrate (Rochelle salt). Near the equivalence point the reaction proceeds very slowly; therefore it is advantageous to titrate without starch indicator until the iodine color remains for at least 2 minutes. McNabb and Wagner[284] added starch near the equivalence point but overcame the difficulty of slow reaction by adding an excess of iodine and determining the excess colorimetrically.

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[280] A. Kurtenacker and E. Fürstenau, *Z. anorg. u. allgem. Chem.*, 212, 289 (1933).

[281] S. Tribalat, *Anal. Chim. Acta*, **1**, 149 (1947).

[282] M. FitzGibbon, *Analyst*, **58**, 469 (1933).

[283] Cf. R. K. Meade, *J. Am. Chem. Soc.*, **21**, 746 (1899); G. B. Frankforter and L. Cohen, *ibid.*, 29, 1464 (1907); E. Rupp, *Arch. Pharm.*, 241, 608 (1903); L. Rosenthaler, *Z. anal. Chem.*, 46, 714 (1907); R. Merville and J. Dequidt, *Bull. soc. pharm. Lille*, **1947**, No. 2, 18, through *Chem. Abstr.*, **42**, 8105 (1948).

[284] W. M. McNabb and E. C. Wagner, *Ind. Eng. Chem., Anal. Ed.*, 2, 251 (1930).

Since trivalent antimony can be determined accurately by titrating in hydrochloric acid solution with bromate, using methyl orange as indicator (p. 513), the iodometric determination is of little practical value.

Pentavalent Antimony: The iodometric titration of antimony(V) is made in strong hydrochloric acid solution like that of arsenic(V).[285] The titration may be used for the determination of sodium after precipitation with potassium pyroantimonate; the method is inexact.

Johnson and Newman[286] recommend the following procedure for potassium antimonate.

Procedure: Dissolve 0.4 g. of the salt in 30 ml. of 1:1 hydrochloric acid. Heat, add 2 ml. of $0.1N$ iodine solution and 0.2 g. of red phosphorus. Heat until the solution is colorless, filter hot on a Gooch crucible, and wash with about 40 ml. of water. To the filtrate and washings add 4 g. of sodium potassium tartrate and, when this has dissolved, neutralize the solution with $5N$ sodium hydroxide solution (about 30 ml.) until it is only very slightly acid. Cool, add 3 g. of sodium bicarbonate, and titrate with $0.1N$ iodine solution with starch as indicator.

Note: This method is to be preferred to that based on iodide reduction in which the reaction (unlike that with arsenic(V)) only goes to completion in concentrated acid solution.

11. Tin. ***Divalent Tin:*** Tin(II) is a good reducing agent and is oxidized quantitatively in acid solution to the quadrivalent form by iodine solution. This is the basis for the iodometric determination of tin.

One of the principal sources of error in the determination is the air-oxidation of tin(II) during the titration. Benas[287] proposed that air be excluded from the solution during titration and that an excess of iodine be added to the tin(II) solution followed by a back-titration with thiosulfate. Borgmann[288] found that the reaction between tin(II) and oxygen is catalyzed by iodide and suggested the use of an alcoholic solution of iodine with cacotheline as indicator. Kolthoff and coworkers[289] found that antimony suppresses the air-oxidation of tin(II) and suggested its addition to the titration solution. Since antimony does not completely eliminate the air-oxidation of tin(II), they also added an excess of iodine to the tin solution and back-titrated with thiosulfate. Okell and Lumsden[290] made a comprehensive study of the errors in the iodometric titration. They found that oxygen dissolved in the iodine solution is the source of error in the direct iodometric titration of tin(II) solutions and that titanium(III) chloride inhibits markedly the air-oxidation of tin(II). In the absence of titanium, low results were obtained if air-containing iodine solution was used. They concluded that the best method for titrating tin(II) is the direct titration using air-free iodine solution. They describe a procedure for preparing air-free iodine solution using boiled distilled water and a stream of carbon dioxide to exclude air. Oxygen is removed readily from the tin(II) solution before titration by adding several small portions of sodium bicarbonate to the acid solution.

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[285] Cf. A. Travers and Jouot, *Compt. rend.*, **184**, 605 (1927); A. Kurtenacker and E. Fürstenau, *Z. anorg. u. allgem. Chem.*, 212, 289 (1933).

[286] E. A. Johnson and E. J. Newman, *Analyst*, **80**, 631 (1955); cf. M. FitzGibbon, *ibid.*, **58**, 469 (1933).

[287] T. Benas, *Chem. Zentr.*, **51**, 957 (1884).

[288] P. J. S. Borgmann, *Ned. Tijdschr. Pharm.*, **8**, 140 (1894).

[289] I. M. Kolthoff and L. B. van Lohuizen, *Pharm. Weekblad*, **54**, 718 (1917); I. M. Kolthoff and R. van der Heijde, *ibid.*, **56**, 1466 (1919).

Iron(II), lead, nickel, zinc, aluminum, cobalt, cadmium, and small amounts of antimony do not interfere. Copper(I) does not interfere. Titanium(III) and large amounts of antimony cause high results if the iodine solution contains air; by using air-free iodine solution, this error is avoided.

Aldehydes and Ketones. Petit[291] described an iodometric procedure based on the titration of tin(II) for the determination of aldehydes and ketones which form insoluble *p*-nitrophenylhydrazones. The aldehydes and ketones are precipitated with *p*-nitrophenylhydrazine, the precipitate is separated by filtration on a sintered-glass filter crucible, dissolved in sulfuric acid or sodium hydroxide, the nitro group reduced to amine with an excess of standard tin(II) solution, and the excess tin(II) titrated iodometrically.

Quadrivalent Tin: The iodometric determination of tin(IV) and total tin in a sample is based on the titration of tin(II). For the reduction of tin(IV) to tin(II), many reagents have been used; among these are lead,[292] nickel,[293] iron,[294] zinc,[295] zinc-lead mixture,[296] aluminum,[297] antimony,[298] and hypophosphorous acid.[299] Of these, lead and nickel are most commonly used. The reduction of the tin is effected by boiling the acid solution with the reducing agent and cooling in an air-free atmosphere. This is maintained by passing carbon dioxide or other inert gas through the flask during the procedure, by attaching to the boiling flask a one-hole stopper through which is inserted a tube the other end of which is placed in a saturated solution of sodium bicarbonate, or by attaching a Göckel-Contat trap (p. 28) containing the bicarbonate solution. The reduction by lead or nickel is stopped by cooling the solution to 10–15°C., whereas the action of hypophosphorous acid ceases on cooling the solution and diluting with air-free water. With the more active metals, such as iron, zinc, aluminum, and antimony, it is necessary to remove any excess before the tin(II) is titrated with iodine.

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[290] F. L. Okell and J. Lumsden, *Analyst*, **60**, 803 (1935).

[291] G. Petit, *Bull. soc. chim. France*, **1948**, 141.

[292] Cf. A. R. Powell, *J. Soc. Chem. Ind.*, **37**, 285 T (1918); G. E. F. Lundell and J. A. Scherrer, *J. Ind. Eng. Chem.*, **14**, 426 (1922); S. G. Clarke, *Analyst*, **56**, 82 (1931); J. A. Scherrer, *J. Research Natl. Bur. Standards*, **8**, 309 (1932); B. L. Clarke, L. A. Wooten, and J. D. Struthers, *Ind. Eng. Chem., Anal. Ed.*, **9**, 349 (1937); G. Norwitz and M. Codell, *Anal. Chim. Acta*, **11**, 33 (1954) (titanium alloys).

[293] Cf. R. L. Hallett, *J. Soc. Chem. Ind.*, **35**, 1087 (1916); L. Hertelendi, *Z. anal. Chem.*, **124**, 277 (1942); T. B. McDow, K. D. Furbee, and F. B. Clardy, *Ind. Eng. Chem., Anal. Ed.*, **16**, 555 (1944); F. H. Edwards and J. W. Gailer, *Analyst*, **69**, 169 (1944); A. C. Simon, P. S. Miller, J. C. Edwards, and F. B.

For a critical survey of the merits of various metals as reductants, the paper by Evans and Higgs[300] should be consulted. These authors consider that nickel is the most satisfactory metal for reducing purposes.

Procedure. Reduction of Tin with Lead: Prepare the sample containing not more than 0.2 g. of tin in 300 ml. of solution containing 10–15 ml. of sulfuric acid and 100 ml. of hydrochloric acid. Transfer the sample to a 500 ml. Erlenmeyer flask and add 2–3 g. of test lead. Insert a stopper fitted with a gas inlet tube for passing a constant stream of carbon dioxide through the flask during the rest of the procedure, or a one-hole stopper fitted with a tube which can be dipped into an air-free saturated sodium bicarbonate solution to seal the solution from air. Gradually heat the solution to boiling and boil

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Clardy, *Ind. Eng. Chem., Anal. Ed.*, **18**, 496 (1946); A. Robertshaw and G. C. Brookfield, *Analyst*, **69**, 340 (1944) (steels).

[294] Cf. I. M. Kolthoff, *Z. anal. Chem.*, **60**, 452 (1921); R. Höltje, *Z. anorg. u. allgem. Chem.*, **198**, 287 (1931); W. A. Dupraw, *Anal. Chem.*, **26**, 1642 (1954) (titanium alloys).

[295] Cf. B. S. Evans, *Analyst*, **52**, 565 (1927); P. E. Winkler, *Bull. soc. chim. Belg.*, **41**, 115 (1932).

[296] Cf. M. Hegedüs, *Z. anal. Chem.*, **110**, 338 (1937); **114**, 200 (1938).

[297] Cf. F. L. Okell and J. Lumsden, *Analyst*, **60**, 803 (1935); R. A. G. de Carvalho, *Anal. Chim. Acta*, **14**, 28 (1956).

[298] Cf. E. Stelling, *J. Ind. Eng. Chem.*, **16**, 346 (1924); C. C. Miller and L. R. Currie, *Analyst*, **73**, 377 (1948); M. L. Malaprade, *Bull. soc. chim., France*, **1951**, 739.

[299] Cf. B. S. Evans, *Analyst*, **56**, 171 (1931); B. S. Evans and D. G. Higgs, *ibid.*, **69**, 201 (1944).

[300] B. S. Evans and D. G. Higgs, *Analyst*, **69**, 291 (1944).

gently (to avoid a large decrease in volume) for 30–40 minutes. Remove the flask from the heat, increase the stream of carbon dioxide to prevent back pressure, or, if the one-hole stopper is used, insert the tube in the saturated bicarbonate solution to seal the flask from the air. After the solution cools somewhat, cool in ice to about 10°C. Add 5 ml. of starch solution and titrate to a permanent blue color with standard iodine solution, keeping the solution air-free by passing a stream of carbon dioxide into the flask during the titration. The equivalent weight of tin is 59.35.

Notes: (1) Unless air-free iodine solution is used, it is necessary to standardize the iodine solution against pure tin treated as in the above procedure. The apparent normality of the iodine solution is slightly higher than theoretical owing to the oxidation of some tin by the air in the iodine solution.

(2) The solution must be free of nitrate, which oxidizes iodide to iodine. Molybdenum, chromium, and vanadium, which are reduced by lead and titrated by iodine, must be absent. Tungsten and large amounts of nickel interfere by coloring the solution and obscuring the end-point of the titration. Moderate amounts of copper are reduced to the metal or the cuprous state and do not interfere; however, if more than about 5 mg. of copper is present uncertain results are obtained because of incomplete reduction. The separation of tin from large amounts of copper can be effected readily by precipitating it with ammonia in the presence of aluminum salts. The metastannic acid is dissolved by digestion with sulfuric acid.

(3) Germanium is reduced to an insoluble compound by lead and does not interfere; however, if iron is used the germanium is only partially reduced to a soluble compound which is reoxidized by iodine and introduces an error.

Procedure. *Reduction of Tin with Hypophosphorous Acid:* Place the solution containing the tin in a 500 ml. Erlenmeyer flask. Add an equal volume of concentrated hydrochloric acid and dilute to about 90 ml. with 1:1 hydrochloric acid. Boil for 1 minute a mixture of 10 ml. of 1:1 hydrochloric acid, 1 ml. of 1 per cent mercuric cyanide solution, and 0.5 g. of sodium hypophosphite, and add it to the tin solution. Stopper the flask with a rubber stopper fitted with a dropping funnel, a glass tube for introduction of carbon dioxide, and a third hole through which a burette tip may be inserted for the titration but which is stoppered with a glass rod. Sweep out the flask with carbon dioxide for 10 minutes, leaving the stopcock on the dropping funnel open to allow the gas to escape. With the gas still flowing, boil the solution for 15 minutes. Close the stopcock and allow the solution to cool under a low pressure of carbon dioxide. Make up a diluting solution by boiling for 10 minutes a mixture of 10 ml. of 4 per cent potassium iodide solution, 20 ml. of 50 per cent citric acid solution, 250 ml. of water, and a few milliliters of 1 per cent starch solution. When both solutions are cold (20°C. or less), add 3 g. of sodium bicarbonate to the diluting solution and add it to the flask through the dropping funnel by removing the glass rod from the stopper of the flask. Insert the tip of the burette containing standard $0.1N$ iodine in this hole in the stopper and titrate the solution to the blue end-point. Run a blank titration and correct the sample titer. The equivalent weight of tin is 59.35.

Notes: (1) Considerable amounts of antimony do not interfere with the determination of tin except that the end-point color fades when antimony is present. The end-point obtained, however, is very sharp. On the other hand, if more than 3 mg. of copper is present the end-point color fades, and the titration is not reliable.

(2) Hypophosphite in acid may also be used to reduce germanium(IV) to germanium(II) and separate it from arsenic which is precipitated as the free element.[301] The reduction is complete by boiling 40–50 minutes. The arsenic

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[301] B. N. Ivanov-Emin, *Zavodskaya Lab.*, **13**, 161 (1947), through *Chem. Abstr.*, 42, 480 (1948).

precipitate is filtered off and the solution reduced again by boiling with hypophosphite for 15–20 minutes. The germanium(II) is titrated iodometrically after the temperature of the solution reaches 20°C. or less to avoid oxidation of the excess hypophosphite.

Wheeler[302] introduced a new method for the determination of tin which is based on the fact that under the proper conditions stannic tin, in the presence of oxalic acid, on treatment with hydrogen sulfide forms a fairly stable compound which can be titrated with iodine solution. Willard and Toribara[303] improved Wheeler's method and developed the procedure given below. The reactions involved in the method are

$$K_6Sn_2(C_2O_4)_7 + 2H_2S \longrightarrow 2K_2SnS(C_2O_4)_2 + 2H_2C_2O_4 + K_2C_2O_4$$

$$2K_2SnS(C_2O_4)_2 + 2I_2 + 2H_2C_2O_4 + K_2C_2O_4 \longrightarrow K_6Sn_2(C_2O_4)_7 + 4HI + 2S$$

Reagents. *Potassium Sulfide Solution:* Dissolve 20 g. of potassium hydroxide in 100 ml. of water and saturate with hydrogen sulfide, keeping the solution cold. Keep the solution under an inert atmosphere to prevent the formation of sulfite and thiosulfate, which are oxidized by iodine in the procedure. The inert atmosphere can be provided by bubbling the solution with carbon dioxide before stoppering the bottle after each use.

Wash Liquid: Dissolve 5 g. of oxalic acid in a liter of water and add potassium oxalate until the pH of the solution is 3.

Procedure: Dissolve the sample containing about 0.15 g. of tin with 2 ml. of 1:1 sulfuric acid and several milliliters of concentrated nitric acid in a 200 ml. electrolytic beaker. Evaporate the solution to dense fumes of sulfuric acid to expel the nitric acid. Cool and add 2–3 g. of potassium oxalate. Wash down the beaker and watch glass with about 20 ml. of wash liquid. Continue adding solid potassium oxalate until the pH is between 2.2 and 2.8. (All of the solid may not dissolve because of the large amount of potassium binoxalate formed.) The following indicators can be used to adjust the pH: xylenol blue, metacresol purple, or thymol blue. Add potassium oxalate until all the red tint disappears.

Dilute the solution to about 60 ml. and heat to 60°C. While stirring, add dropwise 3.5 ml. of potassium sulfide solution. Cover the beaker with a split watch glass because of the gas evolution. Continue heating at this temperature for 5 minutes. Add a few more drops of potassium sulfide solution and heat for 1 minute. (Neither the temperature nor the time is critical; temperatures between 55 and 80°C. and times from 3 to 10 minutes are suitable.) Dilute the solution to about 120 ml. so that no precipitate forms to occlude the sulfur complex. Stirring the solution mechanically, pass a stream of carbon dioxide through it until no test for hydrogen sulfide is shown by lead acetate paper. This requires about 30 minutes. Titrate the solution with standard $0.1N$ iodine solution, adding about 1 ml. in excess. Back-titrate the solution with standard thiosulfate, using starch as indicator. The equivalent weight of tin is 59.35.

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[302] W. C. G. Wheeler, *Analyst*, 63, 883 (1938).

[303] H. H. Willard and T. Y. Toribara, *Ind. Eng. Chem., Anal. Ed.*, 14, 716 (1942).

Notes: (1) Metals which yield precipitates with hydrogen sulfide must be made harmless. If copper and antimony are present, they precipitate as sulfides on addition of the sulfide solution. After the 5 minute heating period, filter the solution hot into a 250 ml. wide-mouthed flask. Wash the container with hot wash solution. Heat the filtered solution to 60° with constant stirring, add 0.5 ml. of potassium sulfide solution, and continue the heating for another minute. Cool the solution to room temperature, pass through carbon dioxide, and carry out the titration as described.

In the presence of much lead and some antimony (lead-bearing metal), dissolve the alloy in nitric acid; antimony and tin remain as precipitated hydrous oxides. Filter off the precipitate and wash with hot water. Decompose the precipitate and filter paper with sulfuric and nitric acids and heat to fumes of sulfuric acid. Add some hydroxylamine sulfate to reduce the antimony to the trivalent state and boil to decompose the excess hydroxylamine. Add potassium chloride with the potassium oxalate to keep the antimony in solution on dilution. Continue the determination as above.

Samples containing much copper are dissolved in nitric acid to separate the tin from copper. The hydrous stannic oxide is filtered off and determined as in the lead-bearing metal except that hydroxylamine and potassium chloride need not be added.

(2) Since the tin is always in the quadrivalent form, no special precautions need be taken to maintain an inert atmosphere. Carbon dioxide is necessary only to remove the excess hydrogen sulfide.

12. Phosphorus.

Elementary Phosphorus: Both red and yellow phosphorus are oxidized to phosphoric acid by potassium iodate in hot acid solution. According to Buehrer and Schupp,[304] the reaction mechanism is very complex and the following reactions are involved:

$$5P + 3IO_3^- + 3H^+ + 6H_2O \longrightarrow {}^3/_2I_2 + 5H_3PO_3 \qquad \text{(slow)}$$

$$2P + 3I_2 + 6H_2O \longrightarrow 6H^+ + 6I^- + 2H_3PO_3 \qquad \text{(rapid)}$$

$$5H_3PO_3 + 2IO_3^- \longrightarrow I_2 + 3H^+ + 5H_2PO_4^- + H_2O \qquad \text{(very slow)}$$

$$H_3PO_3 + I_2 + H_2O \longrightarrow 3H^+ + 2I^- + H_2PO_4^- \qquad \text{(slow)}$$

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O \qquad \text{(instantaneous)}$$

It is probable that the penultimate reaction determines the overall rate of the reaction between phosphorus and iodate, which is given by the equation

$$5P + 5IO_3^- + 5H_2O \longrightarrow {}^5/_2I_2 + 5H_2PO_4^-$$

To determine elementary phosphorus, Buehrer and Schupp refluxed for 3–4 hours under a water condenser the reaction mixture containing about 0.1 g. of phosphorus, 0.8 g. of potassium iodate, 10 ml. of $4N$ sulfuric acid, 65 ml. of water, and 2 ml. of carbon tetrachloride. After this reaction period, the liberated iodine was distilled over into a flask containing a known (but not an excess) volume of standard thiosulfate solution to which was added some cracked ice to prevent loss of iodine. Finally, the iodine was titrated with standard thiosulfate solution.

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[304] T. F. Buehrer and O. E. Schupp, Jr., *J. Am. Chem. Soc.*, 49, 9 (1927).

Phosphorous Acid and Phosphite: The iodometric determination of phosphorous acid was first reported by Rupp and Finck[305] and later improved by Boyer and Bauzil.[306] The determination is based on the slow oxidation of phosphite to phosphate in bicarbonate solution by an excess of iodine solution:

$$H_3PO_3 + I_2 + H_2O \longrightarrow H_3PO_4 + 2HI$$

Under these conditions, hypophosphite remains unchanged and does not interfere with the determination of phosphite.

Procedure: Add the sample solution containing about 0.15 g. of phosphorous acid to a 250 ml. glass-stoppered Erlenmeyer flask. Carefully neutralize and add in excess 50 ml. of $0.2M$ sodium bicarbonate solution saturated with carbon dioxide. Add a measured volume of standard $0.1N$ iodine solution (about 10 ml. excess), and allow to stand for 45–60 minutes. Finally, titrate the excess iodine with standard $0.1N$ arsenite solution. The equivalent weight of H_3PO_3 is 40.99.

Schwicker[307] hastened the oxidation by controlling the alkalinity with ammonium borate, ammonia, or alkali metal hydroxide.

Reagent. *Ammonium Borate Solution:* Dissolve 20 g. of boric acid in 170 ml. of 10 per cent ammonia solution and dilute with water to 1 liter.

Procedure: Treat the phosphite solution with an excess of standard $0.1N$ iodine solution and 5 ml. of ammonium borate solution. After 15 minutes, acidify the solution with $2N$ hydrochloric acid and back-titrate the excess iodine with standard $0.1N$ thiosulfate solution.

Notes: (1) The excess iodine may be back-titrated with standard 0.1 arsenite solution without acidifying the solution.

(2) Raquet and Pinte[308] used borax solution to make the reaction solution alkaline and acidified with acetic acid before titrating the excess iodine with thiosulfate.

Jones and Swift[309] found that in a neutral solution phosphorous acid was oxidized quantitatively by iodine to phosphate in 1 hour:

$$PO_3^{3-} + H_2O + I_3^- \longrightarrow PO_4^{3-} + 2H^+ + 3I^-$$

Hypophosphite does not interfere.

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[305] E. Rupp and A. Finck, *Ber.*, **35**, 3691 (1902); *Arch. Pharm.*, **240**, 663 (1902).

[306] Boyer and Bauzil, *J. pharm. chim.*, (7) **18**, 321 (1918); see also the extensive studies of L. Wolf and W. Jung, *Z. anorg. u. allgem. Chem.*, **201**, 337 (1931), who recommend a similar procedure.

[307] A. Schwicker, *Z. anal. Chem.*, **78**, 103 (1929).

[308] D. Raquet and P. Pinte, *J. pharm. chim.*, (8) **18**, 5, 90 (1933).

[309] R. T. Jones and E. H. Swift, *Anal. Chem.*, **25**, 1272 (1953).

Procedure: Transfer 25 ml. of buffer solution (prepared by mixing sodium dihydrogen phosphate monohydrate, and sodium hydroxide to give a pH of 7.3 ± 0.2) to a 250 ml. iodine flask. Pipette into the flask 25 ml. of the acid solution and add 25 or 50 ml. of $0.1N$ iodine solution (depending on the amount of phosphorous acid present). Stopper the flask, swirl gently, and leave in the dark for 1 hour. Add 5 ml. of $6N$ acetic acid and immediately titrate the excess of iodine with $0.1N$ thiosulfate to the starch-iodine end-point.

Hypophosphite: In acid medium, phosphorous acid is oxidized very slowly but perceptibly by iodine. Under these conditions hypophosphite is oxidized somewhat more readily to phosphorous acid. Wolf and Jung[310] determined hypophosphite by treating the acidified solution with a large excess of iodine and, after a suitable reaction period, adding an excess of sodium bicarbonate and determining the phosphorous acid formed by iodometric oxidation to phosphate.

Procedure: Neutralize the sample solution, and add 10 ml. of 1:9 sulfuric acid and a known excess of iodine solution. Allow the mixture to stand for 10 hours in a glass-stoppered Erlenmeyer flask. Neutralize the solution with a sodium bicarbonate paste (prepared by triturating the solid with water) and finally add 50 ml. of $0.2M$ sodium bicarbonate in excess. Allow the solution to stand 45–60 minutes and titrate the excess iodine with standard $0.1N$ arsenite solution. The equivalent weight of H_3PO_2 is 16.49.

Notes: (1) In a mixture of phosphite and hypophosphite, the phosphite can be determined iodometrically in the alkaline solution and the sum of the phosphite and hypophosphite by the hypophosphite procedure.

(2) Raquet and Pinte[308] shortened the above procedure by warming the reaction mixture and using borax instead of bicarbonate. Their procedure is as follows. To 5 ml. of approximately 1 per cent hypophosphite solution in a glass-stoppered Erlenmeyer flask add 25 ml. of standard $0.1N$ iodine solution and 5 ml. of 10 per cent hydrochloric acid. Stopper and tie the stopper on securely; then warm in a 70° water bath for 15 minutes. Cool, add 10–20 ml. of warm 10 per cent borax solution, and allow to stand for 15 minutes. Acidify the solution with acetic acid and titrate the excess iodine with standard $0.1N$ thiosulfate solution.

Jones and Swift[309] recommend oxidation in a medium $1.5M$ in hydrochloric acid for 3 hours:

$$PO_2^{3-} + H_2O + I_3^- \longrightarrow PO_3^{3-} + 2H^+ + 3I^-$$

The phosphite is then further oxidized to phosphate (p. 325). Mixtures of hypophosphorous and phosphorous acids may be determined by applying this procedure (in which 2 equivalents of iodine are reduced per mole of phosphorous acid and 4 equivalents per mole of hypophosphorous acid) and then applying the procedure for the determination of phosphorous acid (p. 326).

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[310] L. Wolf and W. Jung, *Z. anorg. u. allgem. Chem.*, 201, 337 (1931).

Procedure: Transfer 30 ml. of 6*N* hydrochloric acid to a 250 ml. iodine flask and add 25 ml. of the test solution. Flush the solution and flask with carbon dioxide. Add 50 ml. of 0.1*N* iodine solution, wash down the sides of the flask, stopper, and swirl gently. Place the flask in the dark for 3.5 hours. Add 6*N* sodium hydroxide equivalent to the acid present and swirl gently. Add 25 ml. of the buffer solution (p. 326). Again wash down the sides of the flask and place in the dark for 1 hour. Complete the determination as given on p. 326.

Brukl and Behr[311] determined the sum of the two acids by warming with a known excess of standard iodate solution, which rapidly oxidized both to phosphoric acid, and then titrating the excess of iodate iodometrically. A further sample was then digested with ethanolic potassium hydroxide and filtered (potassium phosphite is virtually insoluble in an ethanolic medium), and the hypophosphite in the filtrate was titrated. The amount of phosphorous acid was obtained by difference.

13. Selenium and Tellurium. ***Selenious Acid and Selenite:*** Two iodometric methods, based on the reduction of selenite to elemental selenium, are commonly used; the reducing agents used are hydriodic acid and thiosulfate, respectively.

(*a*) *Reduction with Hydriodic Acid:* In acid solution, selenite is reduced to selenium by potassium iodide:[312]

$$SeO_3^{2-} + 4I^- + 6H^+ \longrightarrow Se + 2I_2 + 3H_2O$$

The iodine liberated by this reaction is titrated with thiosulfate. Elemental selenium interferes with the observation of the starch-iodine color change. Van der Meulen[313] overcame this difficulty by adding starch as protective colloid before the reduction. The end-point of the titration is marked by a sharp change in color from a dirty brown to a clear red. [Probably it would be better to use a water-insoluble organic solvent instead of starch to detect the end-point of the titration. Authors.] Gooch and coworkers[314] used other modifications of the procedure of Muthmann and Schäfer for the iodometric determination of selenite.

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[311] A. Brukl and M. Behr, *Z. anal. Chem.*, 64, 23 (1924).

[312] W. Muthmann and J. Schäfer, *Ber.*, 26, 1008 (1893).

[313] J. H. van der Meulen, *Chem. Weekblad*, 31, 333 (1934).

[314] F. A. Gooch and W. G. Reynolds, *Am. J. Sci.*, (3) 50, 249 (1895); F. A. Gooch and A. W. Pierce, *ibid.*, (4) 1, 31 (1896).

Procedure: To 20 ml. of selenite solution (approximately 0.05*M*) add 150 ml. of water, 15 ml. of 2 per cent starch solution, 10 ml. of *N* potassium iodide solution, and 10 ml. of 5*N* hydrochloric acid. After a few minutes, titrate the solution with standard 0.1*N* sodium thiosulfate solution, observing the color change against a white background. The equivalent weight of selenite is 19.77.

Notes: (1) According to van der Meulen,[313] if selenate or other oxidizing or reducing substances are present, selenite can be oxidized to selenate with hypobromite (see p. 592); then the selenate can be reduced to selenite by acidifying the solution with hydrochloric acid and adding potassium bromide. The total selenium in the sample is then determined iodometrically by the above procedure.

(2) The method is applicable to the determination of selenium in 18-8 stainless steel [315] and in glass.[316]

(3) McCullough *et al.*[317] recommend that the solution first be boiled to remove dissolved oxygen and an atmosphere of carbon dioxide then be maintained throughout the determination.

(*b*) *Reduction with Thiosulfate:* Norris and Fay[318] employed the following reaction for the determination of selenite:

$$4Na_2S_2O_3 + H_2SeO_3 + 4HCl \longrightarrow Na_2SeS_4O_6 + Na_2S_4O_6 + 4NaCl + 3H_2O$$

An excess of standard thiosulfate solution is added to the acid solution of selenite and immediately back-titrated with standard iodine solution. Coleman and McCrosky[319] made a critical study of the method and found that titrations accurate to 1–2 parts per thousand can be made at room temperature if the excess of thiosulfate is no greater than 5 ml. of 0.1*N* solution.

Procedure: Digest on a hot plate in a 250 ml. flask a mixture of 0.35–0.45 g. of elemental selenium and 5 ml. of 10 per cent sodium cyanide solution until the selenium is completely dissolved as selenocyanate. Dilute the solution to 250 ml. in a volumetric flask and pipette out a 50 ml. aliquot for analysis. Evaporate the solution to about 20 ml. and add 2 ml. of filtered 1 per cent gum arabic solution and 5 ml. of 5*N* hydrobromic acid. The selenocyanate is decomposed with the formation of red selenium, which is kept in the solution by the protective colloid. Bubble the solution for 15 minutes with a rapid stream of air to remove hydrogen cyanide. Add dropwise a saturated potassium bromate solution until most of the selenium is oxidized; then carefully continue the oxidation with 0.1N potassium bromate solution until the red selenium color is discharged. Add a few drops of a saturated alcoholic solution of acetanilide to remove the excess bromine, cover the flask, and heat the solution just to boiling. Dilute the solution to 150 ml., add starch indicator, and allow to cool to 20°C. Add an excess of standard 0.1N thiosulfate solution not to exceed 5 ml. and back-titrate with standard 0.1N iodine solution. The equivalent weight of selenite is 19.77.

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[315] G. G. Marvin and W. C. Schumb, *Ind. Eng. Chem., Anal. Ed.*, **8**, 109 (1936).

[316] A. E. Pavlish and R. W. Silverthorn, *J. Am. Ceram. Soc.*, **23**, 116 (1940).

[317] M. D. McCullough, T. W. Campbell, and N. J. Krilanovich, *Ind. Eng. Chem., Anal. Ed.*, **18**, 638 (1946).

[318] J. F. Norris and H. Fay, *Am. Chem. J.*, **18**, 703 (1896); **23**, 119 (1900). See also F. Foerster, F. Lange, O. Drossbach, and W. Seidel, *Z. anorg. u. allgem. Chem.*, **128**, 318 (1923).

[319] W. C. Coleman and C. R. McCrosky, *Ind. Eng. Chem., Anal. Ed.*, **9**, 431 (1937).

Notes: (1) In order to limit the excess thiosulfate to 5 ml. or less, the following procedure may be used. Add dropwise 1–3 drops of 2.5 per cent potassium iodide solution. As long as selenious acid is present the blue starch-iodine color is produced.

$$H_2SeO_3 + 4HI \longrightarrow Se + 2I_2 + 3H_2O$$

Add thiosulfate in 5 ml. portions until the starch-iodine color does not form on the addition of iodide. Since each mole of selenious acid liberates 4 equivalents of iodine or reacts with 4 equivalents of thiosulfate, no correction is necessary for the iodide added.

(2) When titrations are carried out with 0.01N or more dilute solutions, it is necessary to add potassium iodide to the solution before back-titration to sharpen the end-point.

(3) The procedure has been applied to the determination of selenium in steel[320] and in foods.[321] McNulty[322] has described a routine method for the determination of selenium in horticultural materials. The organic matter is first destroyed and the selenite is titrated as above.

Zirconium and Hafnium: The iodometric selenite titration with reduction by iodide has been applied by Claassen[323] to the determination of zirconium and hafnium. Under proper conditions[324] these metals yield crystalline selenites of the composition $Zr(SeO_3)_2$ or $Hf(SeO_3)_2$. Accurate and reproducible results are obtained.

Procedure: To 100–400 ml. of solution (at room temperature), which should be less than 0.3–0.6N in sulfuric or hydrochloric acid or 0.38N in nitric acid, add 0.5–2 g. of selenious acid in the form of a 10 per cent solution. Heat to boiling and keep on a hot plate for 5–20 hours until the precipitate has become crystalline. Filter by decantation, wash eight times with hot water, then a few times with cold water until the filtrate is free from selenium. Remove most of the precipitate from the filter and transfer it to the precipitation flask. Dissolve in 6 ml. of 1:1 sulfuric acid and 5–10 ml. of 3 per cent sodium fluoride solution by gentle heating. Pass the solution through the filter and wash with hot dilute sulfuric acid containing some fluoride. Collect the filtrate in a 750 ml. Erlenmeyer flask, cool, and dilute to 200–300 ml. Add 10–15 ml. of 2 per cent starch to keep the selenium formed in colloidal solution (p. 327), remove air by successive additions of sodium bicarbonate, and add 2–4 g. of potassium iodide. Titrate after 2 minutes with 0.05–0.1N thiosulfate. One milliliter of 0.1N thiosulfate corresponds to 1.140 mg. of Zr or 2.232 mg. of Hf.

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[320] W. C. Coleman and C. R. McCrosky, *Ind. Eng. Chem., Anal. Ed.*, **8**, 196 (1936).

[321] A. L. Curl and R. A. Osborn, *J. Assoc. Offic. Agr. Chemists*, **21**, 228 (1938).

[322] J. S. McNulty, *Anal. Chem.*, **19**, 809 (1947).

[323] A. Claassen, *Z. anal. Chem.*, **117**, 252 (1939).

[324] S. G. Simpson and W. C. Schumb, *J. Am. Chem. Soc.*, **53**, 921 (1931).

Selenic Acid and Selenates: When selenic acid is boiled with hydrochloric acid the following reaction proceeds quantitatively:

$$H_2SeO_4 + 2HCl \longrightarrow H_2SeO_3 + Cl_2 + H_2O$$

The chlorine is distilled over, collected in a potassium iodide solution, and titrated with thiosulfate. Various authors[325] have obtained good results with this method. Pagel and Miers[326] described a suitable apparatus for carrying out the determination of selenate in the presence of selenite. The sample is refluxed and distilled with constant-boiling hydrochloric acid, a stream of carbon dioxide gas being used to carry over the chlorine.

Hydrobromic acid also quantitatively reduces selenic acid to selenious acid.[327] Soth and Ricci[328] described a simplified distillation apparatus and a suitable procedure for determining selenate by reduction with hydrobromic acid.

Tellurium: Evans[329] developed the following simple procedure for the determination of tellurium in its compounds. Tellurium is readily reduced to the metal by hypophosphorous acid. If gum arabic is added as a protective colloid before the precipitation, the tellurium forms a colloidal suspension which is oxidized immediately and quantitatively in dilute acid solution by iodine.

$$Te + 2I_2 + 3H_2O \longrightarrow H_2TeO_3 + 4I^- + 4H^+$$

The acidity of the solution is controlled with phosphoric acid so that tellurium is oxidized immediately without appreciable oxidation of the excess hypophosphorous acid present in the solution. If the solution is too strongly acid, some hypophosphorous acid is oxidized by iodine; if insufficiently acid, all the tellurium is not oxidized.

Procedure: Neutralize the solution, if necessary, with hydrochloric acid or sodium hydroxide. Add 5 ml. of 1 per cent gum arabic solution and 5 ml. of syrupy phosphoric acid. Dilute the solution to 60 ml. and add 2–3 g. of sodium hypophosphite. Heat the solution to the boiling point and cool. (Just below the boiling point the solution suddenly darkens and, if much tellurium is present, becomes almost black.) When the solution is cool, dilute it with 150 ml. of water and titrate with standard 0.01*N* iodine solution. The solution becomes lighter in color as the titration proceeds. When it is very pale brown, add 4 ml. of carbon tetrachloride and shake vigorously. The aqueous solution should now be decolorized and the carbon tetrachloride layer colored brown. Continue with the titration cautiously, shaking the solution vigorously after each addition of iodine, until the brown color finally disappears and an additional drop of iodine solution colors the carbon tetrachloride a very faint pink. The equivalent weight of tellurium is 31.9.

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[325] F. A. Gooch and P. S. Evans, Jr., *Am. J. Sci.*, (3) **50**, 400 (1895); L. Moser and W. Prinz, *Z. anal. Chem.*, **57**, 301 (1918); R. Doligue, *Ann. chim. anal. chim. appl.*, **18**, 313 (1936).

[326] H. A. Pagel and J. C. Miers, *Ind. Eng. Chem., Anal. Ed.*, **10**, 334 (1938).

[327] F. A. Gooch and W. S. Scoville, *Am. J. Sci.*, (3) **50**, 402 (1895).

[328] G. C. Soth and J. E. Ricci, *Ind. Eng. Chem., Anal. Ed.*, **12**, 328 (1940).

[329] B. S. Evans, *Analyst*, **63**, 874 (1938); cf. *ibid.*, **58**, 452 (1933); L. Vignoli and B. Khaled, *J. pharm. chim.*, **27**, 443 (1938).

Note: Evans obtained good results with samples containing 0.5–10 mg. of tellurium.

For the determination of small amounts of tellurium in high-lead and tin-base alloys, Schaefer[330] dissolves the alloy in hydrochloric acid containing chlorate. The tellurium is precipitated by saturating with sulfur dioxide. The precipitate is dissolved in dilute nitric acid to give H_2TeO_3. Potassium iodide is added in excess and the liberated iodine titrated with thiosulfate.

$$H_2TeO_3 + 4I^- + 4H^+ \longrightarrow Te + 2I_2 + 3H_2O$$

Procedures. Tellurium-Bearing Tin-Base Alloys: Weigh a 5.00 g. sample of the alloy into a 400 ml. beaker. Add approximately 5 g. of potassium chlorate and 50 ml. of concentrated hydrochloric acid (22° Bé.) and heat to the boiling point; if solution is not complete, add more potassium chlorate and repeat the process.

For every volume of solution add 2 volumes of water and boil for at least 5 minutes. Add 10 ml. of a 1 per cent aqueous solution of hydrazine sulfate to the sample containing the tellurium and heat to the boiling point. Precipitate the tellurium by bubbling the sulfur dioxide through this hot solution for at least 15 minutes. After precipitation is complete allow to settle for at least 1 hour, filter on a platinum cone with suction, using Whatman 41H filter paper (or a similar grade), and wash the tellurium with hot water until the chloride ions are completely removed. Dissolve the precipitate from the filter paper with successive portions of warm dilute nitric acid (2:1) to the extent of 25 ml. Wash and dilute the filtrate to approximately 200 ml.

Add about 2 g. of urea to eliminate any small amount of nitrous acid which may be present, cool to room temperature, and add potassium iodide in excess. After 1 minute titrate the liberated iodine with sodium thiosulfate solution, using starch as an indicator. The end-point is permanent for several minutes.

Note: With alloys containing less than 1 per cent of tellurium the use of 0.01 *N* sodium thiosulfate gives an accuracy of 0.02 per cent. For higher percentages of tellurium satisfactory results can be obtained with more concentrated sodium thiosulfate solutions.

Tellurium-Bearing Lead-Base Alloys: Weigh a 5.00 g. sample of the alloy into a 500 ml. flask, add 30 ml. of concentrated sulfuric acid (66° Bé.) and 10 g. of potassium hydrogen sulfate, and heat until all the metal is dissolved and the precipitated salts appear white. Allow to cool, add 80 ml. of water and 10 ml. of concentrated hydrochloric acid, stir the solution well to dissolve the tellurium completely, filter into a 400 ml. beaker, and wash. Add 80 ml. of concentrated hydrochloric acid, dilute the solution to 300 ml. with water, and pass a rapid stream of sulfur dioxide through the hot solution; then proceed as in the case of tin-base alloys.

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[330] R. A. Schaefer, *Ind. Eng. Chem., Anal. Ed.,* 15, 379 (1943).

14. Chromium. *Chromic Acid and Chromate:* The iodometric titration of chromic acid is discussed extensively in connection with the standardization of thiosulfate solutions against potassium dichromate (p. 237). In acid solution, the reaction proceeds according to the equation

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

The rate of this reaction depends markedly on the hydrogen-ion concentration but only slightly on the iodide-ion concentration. Thus, if sufficient acid is added to the reaction mixture, the iodine is liberated so rapidly that it can be titrated immediately with standard thiosulfate solution and accurate results obtained even at high dilutions. As the acidity is increased, however, the air-oxidation of iodide is accelerated; therefore excessive amounts of acid must not be used.

For the analysis of 0.1*N* chromate solutions, it is possible to titrate with thiosulfate immediately after addition of iodide and acid if at least 15 ml. of 4*N* hydrochloric acid and 2 g. of potassium iodide are added per 100 ml. of solution. If only 10 ml. of 4*N* hydrochloric acid is added, accurate results are obtained by waiting 5 minutes before titrating. When the solution is to be titrated after an interval, it should be placed in an iodine flask and set in the dark during the reaction period; otherwise too much iodine is liberated. This is especially important in the titration of dilute chromate solutions.

With 0.01*N* chromate solutions, 3–4 ml. of *N* potassium iodide per 100 ml. of solution is sufficient. If the solution contains 30 ml. of 4*N* hydrochloric acid per 100 ml. of solution, it can be titrated with thiosulfate immediately after mixing. If only 15 ml. of 4*N* hydrochloric acid is used, good results are obtained if the solution is allowed to stand in the dark in a stoppered iodine flask for 5 minutes before being titrated with thiosulfate; if only 10 ml. of 4*N* hydrochloric acid is added, 15 minutes standing time is necessary.

In the titration of 0.001*N* chromate solutions, accurate results are obtained when the titration is made immediately after mixing if at least 20 ml. of 4*N* hydrochloric acid is added per 100 ml. of solution. If 5 ml. of 4*N* hydrochloric acid is added, 15 minutes in the dark is necessary.

In the titration of 0.0001*N* chromate solutions, accurate results are obtained if at least 10 ml. of 4*N* hydrochloric acid is added per 100 ml. of solution and the reaction mixture is allowed to stand for 15 minutes before being titrated.

For the titration of microquantities of chromic acid, the work of Hagen[331] and Gaebler and Baty[332] should be consulted. According to the latter authors, the addition of oxalic acid or tartrate to the acid solution of chromate-iodide accelerates the liberation of iodide by complexing the trivalent chromium formed. Even with trace amounts of chromate, they obtained accurate results by immediate titration of the reaction mixture with thiosulfate, using less acid than given above but adding a small amount of oxalate. They give a procedure for the successive iodometric titration of iodate and chromate in the presence of one another by controlling the pH and using the catalytic effect of oxalate.

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[331] S. K. Hagen, *Z. anal. Chem.*, **95**, 414 (1933).

[332] O. H. Gaebler and M. Baty, *Ind. Eng. Chem., Anal. Ed.*, **13**, 442 (1941).

Kolthoff[333] studied the catalytic effect of various substances in the titration of $0.001N$ chromate solution. Molybdate exerts a double effect; it decreases the rate of reaction of chromic acid with iodide but accelerates a reaction between chromic acid, hydrogen iodide, and thiosulfate which can cause an overconsumption of thiosulfate of up to 80 per cent. This reaction is specially marked when the reaction mixture is exposed to direct sunlight. Ferrous iron acts as a positive catalyst in strongly acid solution but retards the reaction in weakly acid solution.

Trivalent Chromium: Chromium(III) can be oxidized to chromate; after the removal of the excess oxidant, the chromate can be determined iodometrically as previously described. The chromate can, of course, also be titrated with standard reducing agents, e.g., ferrous sulfate (p. 608); this is to be recommended in the presence of much iron. The oxidation can be carried out in acid or alkaline solution. In acid solution ammonium persulfate is often used and the excess is removed by prolonged boiling. Kolthoff and Sandell[334] used potassium bromate as oxidant with a manganous salt as catalyst.

Procedure: To the chromic solution add a little manganous chloride, acidify with sulfuric acid to give a solution about $1N$ in acid, and add 5–10 ml. of 85 per cent phosphoric acid and about 2 g. of pure potassium bromate. Boil for 5–10 minutes to complete the oxidation and decompose the excess oxidant by boiling with 5 g. of ammonium sulfate. The decomposition is rather slow toward the end so, when the development of bromine is only slight, add 10 ml. of N hydrochloric acid and boil until iodine-starch paper no longer turns blue. Cool and titrate the chromic acid in the usual way.

Feigl *et al.*[335] carried out the oxidation in alkaline solution with hydrogen peroxide and removed the excess by boiling with some nickel salt as a catalyst.

Procedure: Make the solution (containing 0.02-0.03 g. of chromium) alkaline with 20 ml. of $2N$ sodium hydroxide, add about 30 ml. of 3 per cent hydrogen peroxide, and boil until after a short time the pure yellow chromate color appears. Add 5 ml. of 5 per cent nickel nitrate solution slowly to avoid excessive foaming. When the first vigorous evolution has stopped, boil for 3 minutes, cool, add 2 ml. of N potassium iodide and 10 ml. of concentrated hydrochloric acid, and titrate with thiosulfate. The method can be used in the presence of proteins such as gelatin.

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[333] I. M. Kolthoff, *Z anal. Chem.*, **59**, 401 (1920).

[334] I. M. Kolthoff and E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **2**, 140 (1930).

[335] F. Feigl, K. Klanfer, and L. Weidenfeld, *Z. anal. Chem.*, **80**, 5 (1930)

Järvinen[336] oxidized the chromium in alkaline solution with bromine water, excess of which was boiled from the acid solution. According to Schulek and Dosza,[337] the method is unsatisfactory because bromide can be further oxidized by chromate; they used a solution of hypobromite and removed the excess with phenol. More recently Schulek and Szakács[338] have described an accurate micro method in which they recommend oxidizing with hydrogen peroxide. To overcome the prolonged boiling necessary to destroy excess, they add chlorine water, followed by potassium cyanide to render the excess of chlorine innocuous.

Procedure: Transfer 20 ml. of the solution containing 0.2–3.5 mg. of chromium to a 100 ml. Erlenmeyer flask fitted with a stopper, add 1–2 ml. of 10 per cent sodium hydroxide solution and 2–6 drops of 3 per cent hydrogen peroxide. Heat to boiling, cool, add 3–7 ml. of fresh, saturated chlorine water, and mix thoroughly. After 2–3 minutes, add 1–2 ml. of fresh 5 per cent potassium cyanide solution and shake while releasing the stopper. Set aside for 2 minutes. Add 10 ml. of 1:1 sulfuric acid and dilute to 40 ml. Add 2 g. of potassium bicarbonate (big crystals if possible) and close the flask. When gas evolution ceases, add 0.2 g. of potassium iodide and titrate with $0.01N$ sodium thiosulfate.

Van der Meulen[339] used potassium persulfate and recommended his method especially for the determination of chromium in presence of manganese. If hydrofluoric acid and phosphoric acid are absent, the manganese is almost completely oxidized to manganese dioxide (cf. p. 373) and only a small amount of permanganate is formed; the latter is reduced to the dioxide with manganous salt after the decomposition of the excess persulfate, and the dichromate is titrated in the filtrate.

Procedure: Heat 25–50 ml. of the solution containing chromium and manganese (which should correspond after oxidation to less than 50 ml. of $0.1N$ dichromate) on a water bath with 2 ml. of $0.1N$ silver nitrate, 2 g. of zinc sulfate, 2 g. of crystalline sodium sulfate, and 1.5 g. of potassium persulfate. At first the trivalent chromium is oxidized, then the separation of manganese dioxide starts, and finally some permanganate is formed. Remove the flask from the bath and boil the mixture smoothly (boiling stones) for about 5 minutes on a wire gauze. Whenever the persulfate has completely decomposed, add 5–10 ml. of *M* manganous sulfate solution and heat further until the supernatant liquid is clear and has assumed a pure yellow color. Filter through a sintered-glass crucible (G4) and wash with a little hot water. Cool, add 10 ml. of *N* potassium iodide and 5 ml. of 6*N* hydrochloric acid, and titrate after some minutes with 0.1*N* thiosulfate. One milliliter of 0.1*N* thiosulfate corresponds to 1.7334 mg. of Cr.

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[336] K. K. Järvinen, *Z. anal. Chem.*, **75**, 1 (1928).

[337] E. Schulek and A. Dosza, *Z. anal. Chem.*, **86**, 81 (1931).

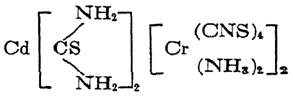
[338] E. Schulek and M. Szakács, *Acta. Chim. Acad. Sci. Hung.*, **4**, 457 (1954).

[339] J. H. van der Meulen, *Rec. trav. chim.*, **51**, 369 (1932).

Note: The sum of manganese and chromium is determined by oxidation in presence of hydrofluoric acid and phosphoric acid (p. 373).

Application of Chromic Titration to Determination of Various Cations: In nitric or sulfuric acid solutions, bismuth is quantitatively precipitated by potassium chromic thiocyanate as $BiCr(CNS)_6$. The precipitate is easy to filter and wash and, after suitable treatment, its chromium can be determined iodometrically as above.[340]

With Reinecke's salt, mercury in hydrochloric acid solution yields a crystalline precipitate of composition $Hg\left(Cr\genfrac{}{}{0pt}{}{(CNS)_4}{(NH_3)_2}\right)$.[341] An iodometric method for its evaluation based on the chromium determination of Kolthoff and Sandell[334] has been developed by Mahr.[342] Copper can be determined by a similar procedure.[343] While only copper and mercury give a precipitate with Reinecke's salt in acid solution, Mahr and Ohle[344] found that in the presence of thiourea other cations precipitated. Cadmium precipitates as



$$Cd\left[CS\genfrac{}{}{0pt}{}{NH_2}{NH_2}\right]_2\left[Cr\genfrac{}{}{0pt}{}{(CNS)_4}{(NH_3)_2}\right]_2$$

This provides a basis for the gravimetric or titrimetric determination by the chromic titration. Cadmium can be separated by this means from many cations, including zinc, and chloride and iodide do not interfere. The original papers should be consulted for details of the methods mentioned.

Application of Chromate Titration to Determination of Metals: The iodometric titration of chromate may be used for the determination of metals, such as barium, strontium, lead, and thallium, which form slightly soluble chromates[345]; bismuth gives erroneous results and cannot be determined in this way. The iodometric titration of chromate is useful also for the rapid determination of soluble sulfates.

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[340] C. Mahr, *Z. anorg. Chem.*, **208**, 313 (1932).

[341] A. Reinecke, *Ann.*, **126**, 113 (1863).

[342] C. Mahr, *Z. anal. Chem.*, **104**, 241 (1936).

[343] C. Mahr, *Z. anorg. Chem.*, **225**, 386 (1935).

[344] C. Mahr and H. Ohle, *Z. anal. Chem.*, **109**, 1 (1937).

[345] E. Rupp, *Z. anorg. Chem.*, **33**, 156 (1902).

Barium: The titrimetric determination of barium as the chromate has been investigated comprehensively.[346] Barium is precipitated in a neutral or acetic acid–acetate buffer medium by the addition of a slight excess of potassium chromate solution. The barium chromate precipitate is filtered off, washed, and dissolved in dilute hydrochloric acid. The chromate is then titrated iodometrically. It is also possible to add an excess of standard potassium chromate solution to precipitate the barium and back-titrate an aliquot portion of the filtrate.[347]

Direct Procedure: Add slowly with stirring an excess of 0.1*N* potassium chromate solution to a suitable amount of neutral barium solution. Allow to stand for 1–3 hours. Filter the solution through close-textured filter paper or a Gooch crucible. Wash the precipitate with ammonium acetate solution (6 g. per liter). Dissolve the precipitate in 50–100 ml. of 1:10 hydrochloric acid, add 2 g. of potassium iodide, and titrate the liberated iodine with standard 0.1*N* thiosulfate solution.

Indirect Procedure: Transfer a suitable amount of neutral barium solution to a volumetric flask. Add slowly, while swirling the solution, a measured volume of standard 0.1*N* potassium chromate solution in excess. Dilute the solution to the volume mark with water, mix thoroughly, and allow to stand for 1–3 hours. Filter the solution through close-textured paper and titrate the excess chromate iodometrically in an aliquot portion of filtrate.

Notes: (1) The precipitation may be made either at room temperature or at elevated temperatures.

(2) If the barium solution contains free acid, its pH should be adjusted to 5–6 with sodium acetate solution.

(3) Even large amounts of calcium do not interfere in the barium determination; however, strontium interferes since its chromate coprecipitates with barium chromate.

(4) Sant[348] prefers to titrate with a standard arsenite solution in presence of a borax–boric acid buffer; the only advantage claimed is that a direct primary standard is used.

Barium in Presence of Strontium. *Procedure:* To a suitable amount of neutral barium solution in a 100 ml. volumetric flask add 10 ml. of 4 *N* acetic acid, 10 ml. of 2*N* sodium acetate, and 20 ml. of water. Mix thoroughly and add, while mixing further, a slight excess of standard 0.1*N* potassium chromate solution. Dilute to the volume mark with water, mix thoroughly, and allow to stand for 1 to 3 hours. Filter the solution through close-textured paper and titrate the excess chromate iodometrically in an aliquot portion of the filtrate.

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[346] For the older literature see R. Fresenius, *Z. anal. Chem.*, **29**, 413 (1890); cf. L. L. de Koninck, *Mineralanalyse*, 1899, p. 400; L. Robin, *Compt. rend.*, **137**, 258 (1903); A. Skrabal and L. Neustadtl, *Z. anal. Chem.*, **44**, 742 (1905); J. L. M van der Horn van den Bos, *Chem. Weekblad*, **8**, 5 (1911)

[347] I. M. Kolthoff, *Pharm. Weekblad*, **57**, 972 (1920).

[348] B. R. Sant, *Z. anal. Chem.*, **148**, 176 (1955).

Note: The barium can be determined also by titrating directly the chromate in the barium chromate precipitate.

Strontium: According to Kolthoff,[347] strontium can be determined in the following way.

Procedure: To 10 ml. of strontium solution in a 100 ml. volumetric flask add 25 ml. of standard 0.1*N* potassium dichromate and then, with constant stirring, enough ammonia to make the solution just turn pure yellow. Add 15 ml. of water to make about 50 ml. of solution. Agitate the solution continuously, add 45 ml. of 95 per cent alcohol and allow to stand for 3–5 hours. Dilute the solution to the mark with alcohol, mix, and filter. Determine the excess chromate in 50 ml. of filtrate by adding potassium iodide, acidifying with 15 ml. of 4*N* hydrochloric acid, and titrating with standard thiosulfate solution.

Notes: (1) The ammonia must not contain any pyridine bases, which cause uncontrollable errors.

(2) In the titration of chromate, the iodide must be added before the solution is acidified; otherwise some chromate may be reduced by the alcohol.

(3) The calcium content of the solution must be less than 10 mg. per 100 ml. Although calcium chromate is soluble in 50 per cent alcohol, it coprecipitates with strontium chromate.

(4) High concentrations of acetate increase the solubility of strontium chromate. Strontium cannot, therefore, be determined in the filtrate from the barium precipitation (cf. p. 336). If barium and strontium are to be determined in the presence of each other, the barium is determined in one portion of sample and the sum of barium and strontium determined on a second portion by the procedure for strontium.

Lead: Lead is precipitated as the chromate by the addition of an excess of potassium chromate or dichromate to an acetic acid-acetate solution. After suitable aging of the precipitate, the solution is filtered. Lead is determined by dissolving the precipitate in acid and titrating the chromate iodometrically. It is possible also to use an excess of standard potassium dichromate solution to precipitate the lead and back-titrate the excess in the filtrate. In general, it is preferable to titrate the precipitate.[349]

Procedure: To 25–75 ml. of lead solution (0.1–0.001*N*) add 10 ml. of 2*N* sodium acetate and 10 ml. of 2*N* acetic acid and dilute with water to 100 ml. Add an excess of potassium chromate or dichromate solution. The lead precipitates quantitatively but the precipitate is too fine to filter. Digest the solution on a hot water bath for about 2 hours, filter, and wash the precipitate with water until the filtrate is free of chromate. Suspend the precipitate in 25 ml. of $2N$ hydrochloric acid or dissolve in 25 ml. of $2N$ perchloric acid. Add 25 ml. of water and 0.5–1 g. of potassium iodide. Titrate the liberated iodine with standard thiosulfate solution. The equivalent weight of lead is 69.07.

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[349] I. M. Kolthoff, *Pharm. Weekblad*, 57, 934 (1920).

Notes: (1) Höll[350] claims that, in order to obtain a quantitative precipitation of lead, the acetate and acetic acid concentration should not exceed 5 per cent and the dichromate concentration should not be less than 3 per cent.

(2) Mercuric mercury is made harmless by the addition of 50 ml. of 5 per cent sodium chloride solution before the precipitation of lead.[351]

(3) Barium is precipitated by the above procedure. A quantitative precipitation of lead chromate without barium is obtained when the precipitation is carried out in a medium which is $0.1N$ in perchloric acid.

(4) Trivalent iron may be prevented from interfering by precipitating in the presence of much acetic acid.[352]

Mercury: Spacu and Dick[353] determined mercury gravimetrically by precipitation with pyridine and dichromate. The precipitate has the formula $[HgPy_2]Cr_2O_7$, in which Py designates pyridine. Furman and State[354] critically investigated and improved the method. They showed that the dichromate in the precipitate can be titrated iodometrically or with ferrous sulfate, and accurate results are obtained for the determination of mercury in mercuric chloride.

Procedure: Weigh 100–200 mg. of mercuric chloride into a 250 ml. beaker and dissolve in 140 ml. of water. Add 10 ml. of 20 per cent ammonium dichromate; then 1 ml. of pyridine[355] while stirring the solution vigorously. After 10 minutes, filter off the yellow precipitate on a sintered-glass crucible. Transfer the precipitate to the crucible with some dichromate-pyridine solution (0.5 g. of ammonium dichromate and 0.5 ml. of pyridine per liter) and wash 6–8 times with acetone. Draw air through the crucible for 5 minutes to evaporate the acetone. Dissolve the precipitate in 50 ml. of $1.2N$ hydrochloric acid, treat with an excess of potassium iodide, and titrate with standard $0.1N$ thiosulfate solution. The equivalent weight of mercury is 33.43.

Notes: (1) Results are accurate to 0.2–0.3 per cent.

(2) Instead of acetone, 80 per cent ethanol may be used but acetone is better.

(3) The dichromate in the precipitate can also be titrated with ferrous sulfate. Dissolve the precipitate in 50 ml. of $2.4N$ hydrochloric acid, add 20 ml. of 25 per cent phosphoric acid and diphenylamine as indicator, and titrate with freshly standardized ferrous solution.

(4) Augusti[356] found that mercuric salts with an alkali metal chromate or dichromate and ammonia form a precipitate having the formula $(Hg_2N)_2CrO_4{\cdot}2H_2O$. This precipitate is used for the determination of mercury.

Sulfate: The iodometric determination of sulfate is based on the titration of chromate. Sulfate is precipitated from an acid solution by the addition of an excess of standard barium solution. The solution is then neutralized with ammonia and the barium ions in solution are precipitated by adding an excess of standard chromate solution. The solution is filtered and the chromate in the filtrate is determined iodometrically.

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[350] K. Höll, *Z. anal. chem.*, **102**, 4 (1935).

[351] H. Funk and J. Schormüller, *Z. anal. Chem.*, **82**, 361 (1930).

[352] H. Funk and O. v. Zur-Mühlen, *Z. anal. Chem.*, **85**, 435 (1931).

[353] G. Spacu and J. Dick, *Z. anal. Chem.*, **76**, 273 (1929).

[354] N. H. Furman and H. M. State, *Ind. Eng. Chem., Anal. Ed.*, **8**, 467 (1936).

[355] It is important to use very pure pyridine, since the presence of other organic bases may yield erratic results.

[356] S. Augusti, *Gazz. chim. ital.*, **65**, 689 (1935); *Chem. Abstr.*, **30**, 2520 (1936).

The barium sulfate need not be filtered off before the excess barium is precipitated with chromate, even though the solubilities of barium sulfate and barium chromate are of the same order of magnitude. The reason is that well-aged crystals of barium sulfate react only very slowly with chromate:

$$BaSO_4\text{ (solid)} + CrO_4^{2-} \rightleftharpoons BaCrO_4\text{ (solid)} + SO_4^{2-}$$

The principle of the method is very old[357] and has been studied extensively. For the sake of simplicity and to avoid the necessity of standard barium and chromate solutions, most of the earlier workers used barium chromate either in a hydrochloric acid solution or as an aqueous suspension. The barium chromate is added to the acid sulfate solution. After complete precipitation of barium sulfate, the solution is neutralized with ammonia and the barium sulfate–barium chromate precipitate filtered off. The chromate in the filtrate corresponds to the sulfate in the sample and is determined iodometrically (or with ferrous solution). This method has been used successfully for the determination of sulfate in natural waters.[358] However, the presence of chromate in solution when the sulfate is precipitated as barium sulfate results in the coprecipitation of chromate or dichromate with the barium sulfate.[359] In principle, therefore, it is better not to use the barium chromate addition method.

Manov and Kirk[359] studied the sources of error in the iodometric determination of sulfate. In addition to the coprecipitation error mentioned above they found that the ammonia used to neutralize the solution should be carbonate-free. In the presence of carbonate, barium chromate reacts according to the equation

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[357] R. Wildenstein, *Z. anal. Chem.*, **1**, 323 (1862); Hinman, *Am. J. Sci. and Arts*, **114**, 478 (1877), through F. P. Treadwell and W. T. Hall, *Analytical Chemistry*, Vol. II, 9th ed., Wiley, New York, 1942, p. 657; L. W. Andrews, *Am. Chem. J.*, **11**, 567 (1889); M. Reuter, *Chem. Ztg.*, **22**, 357 (1898); L. W. Winkler, *Z. anal. Chem.*, **40**, 465 (1901); J. D. Pennock and D. A. Morton, *J. Am. Chem. Soc.*, **25**, 1265 (1903); G. Bruhns, *Z. anal. Chem.*, **45**, 573 (1906); A. Komarowsky, *Chem. Ztg.*, **31**, 498 (1907); G. Romijn, *Pharm. Weekblad*, **45**, 405 (1908); M. Holliger, *Z. anal. Chem.*, **49**, 84 (1910); H. W. Brubaker, *J. Am. Chem. Soc.*, **34**, 284 (1912); I. M. Kolthoff, *Pharm. Weekblad*, **54**, 1013 (1917); *Rec. trav. chim.*, **40**, 686 (1921).

[358] M. D. Foster, *Ind. Eng. Chem., Anal. Ed.*, **8**, 195 (1936).

[359] G. G. Manov and P. L. Kirk, *Ind. Eng. Chem., Anal. Ed.*, **9**, 198 (1937); cf. D. T. Gibson and T. H. Caulfield, *Analyst*, **60**, 522 (1935).

$$BaCrO_4(solid) + CO_3^{2-} \rightleftharpoons BaCO_3(solid) + CrO_4^{2-}$$

At equilibrium at 100°C. the ratio of chromate-ion concentration to the carbonate-ion concentration in the solution is 0.126. Manov and Kirk also found it advantageous to use perchloric acid rather than hydrochloric acid for acidification of the solution because of the possible reduction of chromate by chloride. Belcher and Godbert,[360] however, found no difference whether hydrochloric or perchloric acid was used.

Procedure:[359] To a suitable volume of sulfate solution add hydrochloric acid until its concentration is 0.2–0.3N. Heat the solution to boiling and add slowly a measured volume of standard barium chloride solution until an excess of 50–100 per cent is added. Boil and digest the mixture for 2 hours on a steam bath. Add carbonate-free ammonia until the solution is just alkaline (litmus paper or methyl red indicator), cool, and add an excess of standard chromate solution. Mix the solution, filter and wash the precipitate, and determine the chromate in the filtrate.

Notes: (1) After precipitation of the excess barium with chromate, it is convenient to dilute the mixture to a known volume in a volumetric flask and titrate an aliquot portion of the filtrate.

(2) Instead of titrating the excess chromate iodometrically it is possible to use a standard ferrous sulfate solution with diphenylaminesulfonate as indicator.

(3) Instead of neutralizing the mineral acid with ammonia it is sometimes advantageous to use 5–6 g. of sodium acetate.[361] This is specially recommended when cations are present which are precipitated by ammonia. Copper, zinc, and manganese do not interfere when sodium acetate is used for the neutralization. Ferric iron, aluminum, and chromium, however, interfere since their hydrous oxides, which also form in the acetate medium, absorb chromate.

(4) Carbonate and phosphate which precipitate with barium, and reducing agents which react with chromate, interfere.

(5) Elsermann and Wunderlich[362] recommend a reagent consisting of 20 g. of barium chromate dissolved in 1 liter of 5 per cent perchloric acid. They add an accurately measured volume of this reagent to 250 ml. of the slightly acid sulfate solution and boil for 15 minutes. After having neutralized with ammonia solution, they boil for a further 10 minutes, filter, wash the precipitate with hot water, acidify the filtrate, and titrate the dichromate in the usual way.

15. Vanadium. According to Browning,[363] vanadium(IV) is oxidized by iodine to pentavalent vanadium (vanadate) in alkaline solution. The reduction of the vanadium may proceed to the tri-

[360] R. Belcher and A. L. Godbert, *Analyst,* 66, 289 (1941).

[361] Cf. D. Köszegi, *Z. anal. Chem.,* 77, 203 (1929).

[362] E. Elsermann and G. Wunderlich, *Z. anal. Chem.,* 134, 96 (1951).

[363] P. E. Browning, *Am. J. Sci.,* (4) 2, 185 (1896).

valent state with high concentrations of acid and iodide,[364] but over a wide range of acid and iodide concentrations it stops at the tetravalent state at room temperature.[365] A further complication in the direct determination of vanadium is the induced catalytic air-oxidation of iodide during the reaction of vanadium(V) with iodide. Accordingly, Ramsay[366] developed a simple rapid iodometric method for the determination of vanadium with oxygen excluded, which he found to be accurate to ±1 per cent. Evans[367] did not obtain good results in the direct iodometric determination of vanadate. He, therefore, proposed a modification in which the vanadate–iodide reaction occurs in acid solution, in the absence of air but in the presence of ferrocyanide. The latter precipitates the vanadium(IV) formed and prevents further reduction of vanadium.

Procedure: Place the vanadate solution in a 500 ml. Erlenmeyer flask and make slightly alkaline with sodium hydroxide. Add 5 ml. of freshly prepared 10 per cent potassium ferrocyanide solution followed by 50 ml. of 1:1 hydrochloric acid. Stopper the flask with a three-holed rubber stopper carrying: (1) a carbon dioxide inlet tube which reaches to about $^1/_2$ inch above the solution in the flask, (2) a small dropping funnel, and (3) a removable glass plug. Remove the glass plug and sweep the air out of the flask with a rapid stream of carbon dioxide for 5 minutes. Add 20 ml. of 4 per cent potassium iodide solution and 1 ml. of 10 per cent zinc sulfate solution through the funnel, being careful not to allow the liquid level to fall below the stopcock. Rinse the funnel with 30 ml. of water and add to the solution. Close the stopcock, reinsert the glass plug, shake the flask, and allow to stand for 5 minutes. Replace the glass plug with a burette containing standard 0.01 N thiosulfate solution, open the stopcock on the funnel, and titrate. Toward the end of the titration (N.B.: the color of vanadium ferrocyanide is yellow), add starch through the funnel and complete the titration.

Run a blank with the same amounts of reagents; air need not be excluded. Subtract the blank titer from the sample titer. The equivalent weight of vanadium is 51.0.

Notes: (1) Deshmukh[368] reduces vanadium(V) to vanadium(IV) with sulfur dioxide, adds an excess of iodine, and adjusts the pH to 9–10 with a borax–boric acid buffer while passing nitrogen through the flask. After 15 minutes the excess of iodine is titrated with a standard arsenite solution.

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[364] C. Friedheim and H. Euler, *Ber.*, **28**, 2067 (1895); G. Edgar, *Am. J. Sci.*, (4) **26**, 333 (1908); (4) **27**, 174 (1909).

[365] G. Edgar, *J. Am. Chem. Soc.*, **38**, 2369 (1916).

[366] J. B. Ramsay, *J. Am. Chem. Soc.*, **49**, 1138 (1927); cf. W. C. Bray and J. B. Ramsay, *ibid.*, **55**, 2279 (1933); J. B. Ramsay, E. L. Colichman, and L. C. Pack, *ibid.*, **68**, 1695 (1946).

[367] B. S. Evans, *Analyst*, **63**, 870 (1938).

[368] G. S. Deshmukh, *Chem. Ber.*, **88**, 615 (1955).

Verma and Bhuchar[369] reduce with citrate in acid solution; they state the method is preferable to sulfur dioxide reduction.

Procedure: Transfer the solution containing 4–40 mg. of vanadium pentoxide to an iodine flask, add 1–2 ml. of concentrated sulfuric acid, and dilute to 20–50 ml. Add 10 ml. of 0.6*M* potassium citrate solution, boil for 15–20 minutes (taking care to maintain the volume) while a stream of carbon dioxide passes through the flask. Cool in ice, neutralize with excess of sodium bicarbonate (about 10 g.), add a known excess of standard iodine solution, and titrate with standard sodium arsenite after 1 hour with occasional shaking.

The method is applicable in the presence of arsenic, antimony, and copper.

(2) Methods have been described in which vanadium(V) is reduced to vanadium(II) by suitable metal reductors[370] and is then titrated with a standard iodine solution. Berry,[371] however, reported adversely on these methods.

16. Iron.

Ferric Iron. Iodide reacts with ferric iron according to the equation

$$2Fe^{3+} + 2I^- \rightleftharpoons 2Fe^{2+} + I_2$$

The kinetics of this reaction, which is reversible, was investigated extensively by Hershey and Bray,[372] who found for the equilibrium constant of the reaction at 25°C.

$$K = \frac{[Fe^{2+}]^2[I_2]}{[Fe^{3+}]^2[I^-]^2}$$

the values 1.0×10^4 at ionic strength 0.09 and 1.5×10^5 at ionic strength zero.

According to the equilibrium constant, the reaction from left to right is favored; however, many factors influence the extent to which the reaction proceeds. These must be considered in the quantitative iodometric determination of ferric iron.

(*a*) The solution must be strongly acidic since solutions of ferric iron have a marked tendency to hydrolyze. This hydrolysis reduces the ferric iron concentration and causes the reaction to shift from right to left.

(*b*) Anions which form ferric complexes interfere. Phosphoric acid and pyrophosphates form very stable ferric complexes which do not react with iodide. Small amounts of phosphate and pyrophosphate can be rendered harmless by the addition of much hydrochloric acid. With large amounts the interference cannot be eliminated. Large amounts of sulfate interfere; it is, therefore, better to use hydrochloric rather than sulfuric acid to acidify the solution. Organic acids, such as acetic, oxalic, and hydroxy acids, form ferric complexes but their interference can be eliminated by hydrochloric acid. Finally, it should be mentioned that chloride forms ferric complexes, so very large excesses of hydrochloric acid must be avoided.

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[369] M. R. Verma and V. M. Bhuchar, *J. Sci. Ind. Research (India)*, **14B**, 19 (1955).

[370] K. Someya, *Z. anorg. u. allgem. Chem.*, 169, 293 (1928); cf. *ibid.*, **145**, 168 (1925); **160**, 357 (1927); *Sci. Repts. Imp. Univ. Tôhoku*, **17**, 131 (1928).

[371] A. J. Berry, *Analyst*, **59**, 736 (1934).

[372] A. V. Hershey and W. C. Bray, *J. Am. Chem. Soc.*, **58**, 1760 (1936).

(*c*) Iodide must be present in large excess to favor the reaction from left to right.

(*d*) In acid solution, iodide is air-oxidized; therefore, air in the titration flask should be displaced with carbon dioxide. This can be effected readily by adding a little sodium bicarbonate to the acid solution before adding iodide.

(*e*) The reaction of ferric iron with iodide proceeds at a measurable rate, so it is necessary to allow sufficient time for the reaction to go to completion before the solution is titrated with thiosulfate.

Kolthoff[373] found that the iodometric titration of ferric iron at room temperature is suitable for analytical work if the following experimental conditions are used. With a 0.25N ferric solution, it is necessary to have about 2 ml. of 4N hydrochloric acid per 10 ml. of solution and about 1.5 g. of potassium iodide. The solution should be allowed to stand in a stoppered flask for 5 minutes before the liberated iodine is titrated. With more dilute solutions of ferric iron it is better to allow the solution to stand for 15 minutes before titrating. If 3 g. of potassium iodide is used, the time may be reduced to 10 minutes. Even 0.001N ferric solutions can be titrated accurately provided that the solution is 0.1N in hydrochloric acid, at least 5 ml. of N potassium iodide is added per 50 ml. of solution, and the reaction mixture is allowed to stand 30 minutes before the titration.

Mohr[374] accelerated the ferric-iodide reaction by heating the mixture to 50–60°C.; then the solution was cooled and titrated. Kolthoff found the following procedure to be effective and more rapid than the procedure at room temperature.

Procedure: Treat the ferric solution, 0.1N in hydrochloric acid, with 1–2 g. of potassium iodide and titrate with thiosulfate after 3 minutes. After the starch-iodine is decolorized, heat the solution quickly to 50°C. and titrate directly to the end-point. No iodine is lost with rapid heating because the small amount of iodine liberated on heating is held strongly by the excess iodide.

Note: Hahn and Windisch[375] utilized the catalytic action of copper salts to accelerate the ferric-iodide reaction at room temperature. The presence of moderate amounts of sulfate necessitates the use of higher concentrations of acid and iodide, and the end-points are less permanent. If 200 mg. or more of cuprous iodide is added per 100 ml. of solution, sharp, stable, and accurate end-points are obtained in the titration of the liberated iodine with thiosulfate even when large concentrations of sulfate are present.

Ferrous Iron. As stated above, the reaction of ferric iron with iodide is reversible. Thus, if a ferrous solution is treated with iodine, it is partially oxidized to ferric. If the ferric ion is removed from the solution by complex formation, the oxidation can be made to proceed quantitatively. Topf[376] used a hot acetic acid solution for this purpose. Job[377] and Romijn[378] used pyrophosphate to complex ferric iron and titrated ferrous iron directly with iodine. According to Kolthoff,[379] difficulty is encountered from air-oxidation because of the increased reducing power of ferrous in the presence of the complexing agent. The following procedure yields good results.

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[373] I. M. Kolthoff, *Pharm. Weekblad*, 58, 1510 (1921).

[374] F. Mohr, *Ann.*, 113, 260 (1860).

[375] F. L. Hahn and H. Windisch, *Ber.*, 56B, 598 (1923); cf. K. Rosenmund, *Apoth. Ztg.*, 41, 695 (1926); F. L. Hahn, *Anal. Chim. Acta*, 3, 65 (1949); E. W. Hammock and E. H. Swift, *Anal. Chem.*, 25, 1113 (1953).

[376] G. Topf, *Z. anal. Chem.*, 26, 300 (1887); cf. E. Rupp, *Ber.*, 36, 164 (1903).

[377] A. Job, *Compt. rend.*, 127, 59 (1890).

Procedure: To the ferrous solution in a glass-stoppered flask, add 5 ml. of 4*N* sulfuric acid and two 250 mg. portions of sodium bicarbonate to remove air. Add 5 g. of powdered sodium pyrophosphate, stopper the flask, and swirl the solution to dissolve the salt. Add an excess of standard iodine solution and back-titrate with standard thiosulfate solution.

Notes: (1) The accuracy is about 1–2 per cent.

(2) Because of the many good methods available for the determination of ferrous iron, the iodometric method is of little practical interest. However, since iodine is a very mild oxidant, the iodometric titration is of value in the determination of ferrous iron in the presence of organic substances. Extensive investigations of the application of the iodometric ferrous determination to pharmaceutical products have been carried out by Szebellédy.[380]

Ferricyanide. The iodometric titration of ferricyanide was mentioned briefly in connection with the standardization of thiosulfate solution (p. 236). The reaction

$$2Fe(CN)_6^{3-} + 2I^- \rightleftharpoons 2Fe(CN)_6^{4-} + I_2$$

is reversible. In strong acid solution the reaction proceeds from left to right but is reversed in neutral solution. Thus, ferricyanide can be determined iodometrically in strongly acid solution.[381] It is possible, also, to remove ferrocyanide from solution as the slightly soluble potassium zinc ferrocyanide by adding a zinc salt and thereby shifting the equilibrium from left to right even in very weakly acid solution.[382]

Procedure. (*a*) *In Acid Solution:* To 25 ml. of ferricyanide solution add 10 ml. of *N* potassium iodide and 5–20 ml. of 25 per cent hydrochloric acid. After half a minute, titrate with standard thiosulfate solution.

(*b*) *With Zinc Salt:* To 25 ml. of ferricyanide solution add a little 4*N* hydrochloric acid, 10 ml. of *N* potassium iodide, and, half a minute later, 10 ml. of 25 per cent zinc sulfate solution. After a minute, titrate the solution with standard thiosulfate solution. Add starch near the end-point and titrate until the starch-iodine color no longer appears. If the reagents are free of iron the solution is colorless and the precipitate pure white at the end-point.

Ferrocyanide. A critical investigation of the iodometric titration of ferrocyanide was made by Englis and Becker.[383] They found that ferrocyanide is oxidized quantitatively to ferricyanide within 15 minutes by iodine if the ferricyanide concentration is kept less than $0.01M$, if the oxidation is carried out in a mixture of disodium hydrogen phosphate and acetic acid, and if at least 65 per cent excess of iodine is added.

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[378] G. Romijn, *Pharm. Weekblad*, **48**, 996 (1911).

[379] I. M. Kolthoff, *Z. anal. Chem.*, **60**, 453 (1921).

[380] L. Szebellédy, *Z. anal. Chem.*, **81**, 26 (1930).

[381] I. M. Kolthoff, *Z. anal. Chem.*, **60**, 454 (1921); *Pharm. Weekblad*, **59**, 66 (1922).

[382] F. Mohr, *Ann.*, **105**, 60 (1858); cf. E. Müller and O. Diefenthäler, *Z. anorg. Chem.*, **67**, 418 (1910); M. Kohn, *Anal. Chim. Acta*, **10**, 405 (1954).

[383] D. T. Englis and H. C. Becker, *Ind. Eng. Chem., Anal. Ed.*, **15**, 252 (1943).

Procedure: Place 25–50 ml. of the neutral ferrocyanide solution, containing not over 1.5 meq. of ferrocyanide, in a 250 ml. glass-stoppered flask. Add 25 ml. of 10 per cent disodium hydrogen phosphate dodecahydrate (or 25 ml. of 3 per cent potassium fluoride), 25 ml. of 20 per cent acetic acid, and 25 ml. of standard $0.1N$ iodine solution. Stopper the flask and set in the dark for 15–20 minutes. Add 100 ml. of water and titrate the excess iodine with thiosulfate to the starch end-point.

Note: Since the iodometric determination of ferricyanide is simple and exact, Lang[384] oxidizes ferro- to ferricyanide and titrates the ferricyanide as described earlier.

Determination of Reducing Sugars with Ferricyanide: Ferricyanide for the oxidation of reducing sugars was used originally by Gentele.[385] Although the reaction is empirical and lacks specificity,[386] the method has been found useful in biochemistry.[387]

The method has been subjected to critical study by Blom and Rosted[388] and compared with other methods. They consider that methods based on the reduction of copper salts are to be preferred since ferricyanide oxidized many nonsugar substances which copper does not attack at all.[389]

It is perhaps of interest to quote the remarks of Blom and Rosted concerning their survey of various methods: "When looking back on it now we feel almost tempted to say with Jessen-Hansen[390] that if we had foreseen the difficulties which later appeared in this investigation it is perhaps doubtful that we should ever have undertaken it."

Zinc: Lang[391] developed a method for iodometric zinc determination based on the reaction

$$3Zn^{2+} + 2K^{+} + 2Fe(CN)_6^{3-} + 2I^{-} \longrightarrow K_2Zn_3(Fe(CN)_6)_2 + I_2$$

The conditions are chosen so that the side reaction of ferrocyanide with iodine is suppressed.

Procedure: To the neutral zinc solution (nitrate or sulfate) containing less than 0.45 g. of zinc, add 5–10 g. of potassium sulfate. Dilute to about 100 ml.

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[384] R. Lang, *Z. anorg. u. allgem. Chem.*, **138**, 271 (1924).

[385] J. G. Gentele, *Dinglers Polytech. J.*, **152**, 68, 139 (1859); cf. C. Stahlschmidt, *Ber.*, **1**, 141 (1868); N. Jarugi and G. Nicchiotti, *Gazz. chim. ital.*, **27**, II, 131 (1897).

[386] F. Mohr, *Lehrbuch der chemisch-analytischen Titriermethoden*, 2nd ed., Vieweg, Braunschweig 1862, p. 284; J. Quincke, *Z. anal. Chem.*, **31**, 31 (1892).

[387] H. C. Hagedorn and B. N. Jensen, *Biochem. Z.*, **135**, 46 (1923).

[388] J. Blom and C. O. Rosted, *Acta Chem. Scand.*, **1**, 32 (1947).

[389] Cf. A. Fujita and D. Iwatake, *Biochem. Z.*, **242**, 43 (1931).

[390] H. Jessen-Hansen, *Compt. rend. trav. lab. Carlsberg*, **15**, 3 (1923).

[391] R. Lang, *Z. anal. Chem.*, **79**, 161 (1929); **93**, 21 (1931).

and dissolve the salt by heating. Cool, add 2 g. of potassium iodide, starch solution, and 0.2M potassium ferricyanide (66 g. per liter) in portions of about 2 ml. After each addition titrate with 0.1N thiosulfate until the color almost disappears. So long as the precipitate remains white with the addition of 1 drop, zinc remains in solution. When it is yellow, all the zinc has precipitated and ferricyanide is present in excess. Titrate immediately until the blue color does not return for 30 seconds.

The precipitate has not exactly the above composition, and an empirical equivalent weight of 99.70 is used instead of the theoretical value of 98.05. Each milliliter of 0.1N thiosulfate corresponds to 9.97 mg. of zinc.

Notes: (1) Raadsveld[392] tested the Lang method on pure zinc solutions and found a factor of 9.91 which was not wholly constant but varied between 9.86 and 10.02. The method is not recommended for exact determinations but is useful for rapid work.

(2) Sulfuric acid solutions of zinc are neutralized with potassium hydroxide or carbonate (not with the sodium salts) until a permanent precipitate appears, which is then dissolved with drops of sulfuric acid. Chloride interferes but can be removed by fuming with sulfuric acid.

(3) The addition of the large amount of potassium sulfate causes a rapid equilibrium in the precipitation of zinc.

(4) Large amounts of alkali chloride, fluoride, phosphate, acetate, and oxalate are troublesome; about 1 g. of these has no influence. Small amounts of tartrate interfere.

(5) Magnesium, aluminum, and alkaline earths do not interfere. The last are precipitated as sulfate but, if less than 0.1 g. is present, it is unnecessary to filter. Large amounts of ferric salts do not interfere if the solution is neutralized with bicarbonate and an excess of potassium bifluoride is added. If copper is present, it can be determined iodometrically first, followed by the zinc determination. Cuprous iodide does not interfere; mercury and silver are bound as iodide. Less than 20 mg. of manganese does not interfere, but larger amounts must be removed as must cadmium, nickel, and cobalt.

(6) Lang[393] modified his method so that it can be carried out in moderately acid solution. The advantage is that thiocyanates, bromides, nitrates, and salts of weak acids do not interfere.

Procedure: Neutralize the chloride-free solution (containing 0.3–0.4 g. of zinc and 3–5 ml. of sulfuric acid) with ammonia to methyl orange indicator. Acidify distinctly with sulfuric acid, dilute to 100 ml., and add 2 g. of potassium iodide and starch. The method is completed as for neutral solutions.

The procedure is also suitable for dilute solutions; with an end-volume of 150 ml., 0.02N thiosulfate solutions can be used. Thorium salts do not interfere, nor do several grams of uranyl sulfate. Molybdate can be rendered harmless by addition of phosphoric acid.

(7) Van der Meulen[394] claims that the reaction is stoichiometric if carried out in the following way. To 50 ml. of the zinc solution in N hydrochloric acid add 100 ml. of water, 2 g. of potassium chloride, 20 ml. of 0.1M potassium ferricyanide solution, and, after 3 minutes of standing, 10 ml. of 0.5M barium acetate solution, 5–10 drops of 0.5M sodium sulfate solution, and 2 ml. of N iodide. Titrate the iodine with 0.05N thiosulfate.

(8) Lang and Reifer[395] have described methods for the determination of zinc, copper, and iron in the presence of each other.

(9) The iodometric zinc titration has also been applied to the determination of sodium after precipitation as the zinc uranyl acetate.[396]

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[392] C. W. Raadsveld, *Chem. Weekblad,* **32,** 655 (1935).

[393] R. Lang, *Z. anal. Chem.,* **93,** 21 (1933).

[394] J. H. van der Meulen, *Chem. Weekblad,* **38,** 125 (1941).

[395] R. Lang and J. Reifer, *Z. anal. Chem.,* **93,** 161 (1933).

[396] R. Lang and G. Mück, *Z. anal. Chem.,* **93,** 100 (1933).

(10) Casto and Boyle[397] apply Lang's method to the determination of zinc in magnesium alloys.

Procedure: Dissolve the alloy in dilute (1:6) sulfuric acid. If copper is present, boil the solution with 5–10 g. of test lead for 15 minutes. Filter through fast paper and wash with water. To the filtrate add 10 mg. of manganese as manganous sulfate and 1 g. of ammonium persulfate and boil for 30 minutes. Filter the hot solution through a porous porcelain crucible and wash with water, keeping the final volume to less than 150 ml. To the filtrate add 10 ml. of 10 per cent sodium or ammonium citrate solution for every milligram of iron in the solution and add ammonia until the solution is alkaline to methyl orange. Add sulfuric acid until the solution is distinctly acid to methyl orange. The volume of the solution should not exceed 200 ml. at this point. Cool to room temperature, add 1–2 g. of potassium iodide, set aside for 10 minutes, add starch solution and just discharge the blue color with thiosulfate. Continue to titrate the zinc by the method of Lang.

17. Copper. Cupric salts react with iodide as follows:

$$2Cu^{2+} + 4I^- \rightleftharpoons 2CuI + I_2$$

In 1854, de Haen[398] proposed a determination of copper in which the iodine liberated by the above reaction was titrated with sulfurous acid by the Bunsen method. Mohr replaced sulfurous acid with thiosulfate. The reaction between cupric ions and iodide is reversible.[399]

The equilibrium constant of the reaction,

$$K = \frac{[Cu^{2+}][I^-]^2}{[I_2]}$$

has been studied by many workers, and has been estimated as 1.17×10^{-4} to 1.64×10^{-4} at 25°C.[400] and 1.03×10^{-4} to 1.05×10^{-4} at 20°C.[401] Kolthoff[402] calculated from other data[403] a value of about 1.8×10^{-4}.

The value of the equilibrium constant allows the conditions under which copper can be titrated to be theoretically established. Moser[404] and Gooch and Heath[405] studied the conditions from a practical viewpoint.

According to Moser, the amount of potassium iodide must be at least four times the amount required stoichiometrically. The results are lower in neutral than in acid solutions. He recommended that a little sulfuric acid be used; hydrochloric acid interfered by dissolving the cuprous iodide. This explanation is incorrect and the error is caused by complex formation between chloride and copper ions. Kolthoff[406] found that small amounts of hydrochloric acid do not interfere. Gooch and Heath studied the influence of the iodide concentration, the acidity, and the dilution. The results were the same in neutral and in acid media; the iodide should be present in 40–60 times the theoretical amount. Kolthoff[406] found that a small amount of acid accelerated the reaction slightly without affecting the final values.

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[397] C. C. Casto and A. J. Boyle, *Ind. Eng. Chem., Anal. Ed.*, 15, 623 (1943).

[398] E. de Haen, *Ann.*, 91, 237 (1854). For a complete review of the literature, see B. Park, *Bull. Michigan Coll. Mining and Technol.*, 5, No. 1 (1931); *Ind. Eng. Chem., Anal. Ed.*, **3**, 77 (1931).

[399] M. Traube, *Ber.*, **17**, 1064 (1884).

[400] W. C. Bray and G. M. McKay, *J. Am. Chem. Soc.*, **32**, 1707 (1910).

[401] P. P. Fetodieff, *Z. anorg. u. allgem. Chem.*, **69**, 22 (1911).

[402] I. M. Kolthoff, *Rec. trav. chim.*, **46**, 153 (1926).

[403] P. A. Shaffer and A. F. Hartmann, *J. Biol. Chem.*, **45**, 349 (1920/1).

[404] L. Moser, *Z. anal. Chem.*, **43**, 597 (1904).

[405] F. A. Gooch and F. H. Heath, *Z. anorg. Chem.*, **55**, 119 (1907).

Procedure: To the copper solution add 3–5 ml. of 4*N* sulfuric acid and 1.5–2 g. of potassium iodide, dilute to 100 ml., and titrate immediately with thiosulfate.

Notes: (1) Titration in acid solution is said[407] to yield high results because of air-oxidation of cuprous iodide. In 0.2*N* sulfuric acid and 0.4*N* acetic acid, the errors are 0.2 and 0.1 per cent respectively. In neutral or very slightly acid solution (pH 3–4), theoretical values are obtained if the iodide concentration is at least 4 per cent.

(2) Caldwell[408] found that cupric iodide could adsorb iodine. He showed that on addition of an alcoholic shellac solution the precipitate is altered and loses its property of adsorbing iodine. The solution is titrated to near the end-point and then 0.5–1 ml. of 4 per cent alcoholic solution of shellac is added with shaking. After 20–30 seconds the titration is completed. The precipitate has a surface color in presence of iodine.

(3) Hahn and Clos[409] recommended the titration in only slightly acid solution. They acidified 20 ml. of solution with 1 ml. of 2*N* acetic acid and used benzene instead of starch as indicator. The iodine was shaken out so that equilibrium was established more rapidly and the color change was very sharp.

(4) In the titration of dilute solutions (less than 0.02*M*), the color of iodine-starch keeps returning toward the end of the titration. The titration must be continued until the solution remains colorless for 5 minutes. Since the rate of reaction alters with the square of the iodide concentration, a large excess of iodide is still necessary for dilute solutions (about 2 g. per 50 ml. solution).[410]

When a considerable excess of sodium bromide is added to a neutral or slightly acid solution of copper(II), the latter is converted to $(CuBr_4)^{2-}$, which can be titrated and reduced directly with thiosulfate.[411]

$$2(CuBr_4)^{2-} + 2S_2O_3^{2-} \longrightarrow 2(CuBr_4)^{3-} + S_4O_6^{2-}$$

A trace of potassium iodide and 2 ml. of starch are added to detect the end-point, which is marked by the disappearance of the blue color.

[406] I. M. Kolthoff, *Pharm. Weekblad,* 55, 1338 (1918).

[407] S. Popoff, M. Jones, C. Tucker, and W. W. Becker, *J. Am. Chem. Soc.*, 51, 1299 (1929).

[408] J. R. Caldwell, *J. Am. Chem. Soc.*, 57, 96 (1935).

[409] F. L. Hahn and H. Clos, *Z. anal. Chem.*, 79, 32 (1929).

[410] For microdetermination, see C. Dahl, *Tidskr. Kemi Bergvesen*, 7, 8 (1927); *Chem. Abstr.*, 22, 2526 (1928). For the determination of organic copper salts, see M. Uschakow, *Z. anal. Chem.*, 75, 228 (1928).

[411] K. Erler, *Z. anal. Chem.*, 129, 93 (1949).

Procedure: Add the neutral or slightly acid copper solution (2–200 mg. of copper) to 10–20 ml. of a saturated solution of sodium bromide. Titrate with standard thiosulfate, taking care to add the titrant slowly as the end-point is approached.

Note: The method may be used for the indirect determination of sulfite or tin(II) by adding an excess of a standard copper solution and then titrating the excess.

Copper in Ores: For the determination of copper in presence of iron and arsenic, e.g., in copper pyrites, Park[412] successfully used a mixture of two buffer systems (hydrofluoric acid-fluoride and biphthalate) to establish the acidity at which arsenic acid did not react with iodide, while fluoride complexed ferric iron. Crowell *et al.*[413] found that fluoride alone served for both purposes because the hydrofluoric acid–fluoride system is a good buffer. They neutralized the solution with ammonia until a slight excess was present and added 2 g. of ammonium bifluoride and 3 g. of potassium iodide. The pH at the end-point is about 3.3.

Procedure:[412] Weigh about 1 g. of finely ground material into a 150 ml. beaker, add 20 ml. of concentrated nitric acid, and warm until all the copper is in solution. Evaporate to a volume of 5 ml., add 25 ml. of water, and boil to bring all soluble material into solution and to expel nitrogen oxides. Filter on a small filter paper and collect the filtrate in a 250 ml. Erlenmeyer flask (if the residue is small and light-colored, omit the filtration). Wash the residue thoroughly with hot 1 per cent nitric acid. Concentrate the filtrate to 25 ml., cool, and add dilute ammonium hydroxide solution dropwise to precipitate all the iron, being careful to avoid an excess; the liquid should smell faintly of ammonia. Add 2 g. of ammonium bifluoride, shake to dissolve ferric hydroxide, and add 3 g. of potassium iodide. Titrate immediately with 0.1*N* thiosulfate, using 3 ml. of 0.2 per cent starch solution as indicator.

Notes: (1) It is preferable to standardize the thiosulfate solution against pure copper (p. 240).

(2) Approximately 1 g. of ammonium bifluoride should be added for each 0.1 g. of iron present. Aluminum forms a slightly soluble complex fluoride, so that, if large amounts are present, more bifluoride must be added. Manganese alone does not interfere, but if iron is also present the results are high. Martin[414] states that the optimum pH of 3.5–4.0 is too critical to rely on adding ammonia until a faint smell is obtained. He uses methyl orange indicator and adds ammonia solution until the color changes from purple to green (owing to the screening effect of the cupric ion). The addition of ammonium bifluoride causes the purple color to return. The end-point is from blue to pink.

(3) In the presence of antimonate, aluminum, calcium, and ferric iron, low

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[412] B. Park, *Ind. Eng. Chem., Anal. Ed.*, **3**, 77 (1931).

[413] W. R. Crowell, T. E. Hillis, S. C. Rittenberg, and R. F. Svenson, *Ind. Eng. Chem., Anal. Ed.*, **8**, 9 (1936).

[414] R. B. Martin, *Analyst*, **80**, 318 (1955).

results may be found. Crowell and Spiher[415] evaporated the copper solution to fuming with excess sulfuric acid. Under such conditions 0.3 g. of aluminum does not interfere. Calcium or iron up to 0.3 g. can be tolerated provided that the calcium sulfate is filtered off before addition of ammonia and bifluoride. If less than 0.1 g. is present, filtration is unnecessary. Up to 0.2 g. of arsenic does not interfere, but only 20 mg. of antimony can be tolerated.

(4) A method for the determination of copper in sulfide ores after dissolution in perchloric acid has been described.[416]

(5) Matveev and Kazakerich[417] precipitate copper sulfide with thiosulfate after dissolution of the ore. The precipitate is dissolved in nitric acid and treated with a solution containing urea, lead nitrate, potassium iodide, potassium bromide, and potassium thiocyanate; the liberated iodine is then titrated. Very accurate results are claimed for this method.

The "short iodide" method for the rapid determination of copper in ores[418] was modified by Willcocks[419] to make it simpler and more rapid and allow recovery of potassium iodide in used solutions. The modified procedure avoids the interference of manganese because the pH is low enough to prevent the precipitation of manganous hydroxide.[420] Magnesium, which has been observed to cause low results for copper by the usual method,[421] does not interfere.

Procedure: Weigh a suitable amount (0.25–1.0 g.) of powdered copper ore into a Phillips beaker and add 20 ml. of acid mixture (equal volumes of concentrated hydrochloric acid, concentrated nitric acid, water, and 1:1 sulfuric acid). Cover the beaker with a ribbed watch glass and boil the solution on a hot plate (surface temperature about 300 °C.) until fumes appear. Fume for 10 minutes or longer, depending on the ore. Cool the solution and dilute to about 35 ml. with water. Boil for 5 minutes. Cool and add about 2 g. of sodium or ammonium fluoride. Cool to below 25°. Add 25 ml. of solution containing 7.5 g. of potassium iodide and 6.25 g. of anhydrous sodium acetate. Titrate at once with standard thiosulfate, using starch as indicator.

Notes: (1) Some ores containing much shale give a dark-colored residue which interferes with the starch end-point. The residue may be decolorized by adding a few drops of nitric acid or of 10 per cent perchloric acid in nitric acid during the initial fuming of the sample. An alternative method is to add 25 ml. of 60 per cent perchloric acid to each liter of the acid mixture used to decompose the ore.

(2) It is possible to recover the potassium iodide. About 95 per cent recovery has been reported and repeated recovery does not cause any deterioration of the reagent. The original paper[419] should be consulted for details.

[415] W. R. Crowell and A. T. Spiher, *Ind. Eng. Chem., Anal. Ed.*, **12**, 147 (1940).

[416] A. Goetz, H. Diehl and C. C. Hach, *Anal. Chem.*, **21**, 1520 (1949).

[417] N. I. Matveev and N. E. Kazakerich, *Zavodskaya Lab.*, **21**, 405 (1955).

[418] W. R. Mott, *Chemist Analyst*, **No. 5**, 7 (1912).

[419] R. G. W. Willcocks, *J. Appl. Chem.* (*London*), **2**, 608 (1952).

[420] E. T. Pinkney, R. Dick, and R. S. Young, *J. Soc. Chem. Ind.*, **66**, 342 (1947).

[421] S. B. Wallace, private communication.

Copper Titration with Thiocyanate and Iodide: Bruhns[422] found that considerably less iodide is required if potassium thiocyanate is also used as reagent. The favorable effect is said to be due to the fact that copper thiocyanate is 10 times less soluble than cuprous iodide, but this does not accord with published solubility product figures. In the copper titration, a large excess of thiocyanate over iodide is used; this may account for the fact that copper thiocyanate rather than copper iodide precipitates. When a little iodide and much thiocyanate are added to a cuprous solution all the copper is precipitated as thiocyanate; during the titration, iodine is further converted to iodide, which again reacts and so on. With the small solubility of cuprous thiocyanate, the cuprous concentration during the titration is much smaller than in the presence of iodide alone and the reaction can be quantitatively completed much more quickly. Kolthoff[423] has thoroughly examined the Bruhns method. If thiocyanate and iodide are added to the neutral copper solution, acid being added afterwards, the consumption of thiosulfate is low because a little thiocyanate is oxidized by iodine to cyanide and sulfate. If the acid is added first, the oxidation is avoided (iodide can also be added before the acid but thiocyanate must be added last). If the solution containing copper, acid, iodide, and thiocyanate is allowed to stand before titration, the thiosulfate consumption is always decreased. The phenomenon has been explained in the following way.[424] In the mixture the reactions are

$$2Cu^{2+} + 4I^- \rightleftharpoons Cu_2I_2 + I_2$$

$$Cu_2I_2 + 2CNS^- \rightleftharpoons Cu_2(CNS)_2 + 2I^-$$

$$2Cu^{2+} + 4CNS \rightleftharpoons Cu_2(CNS)_2 + (CNS)_2$$

The third reaction leads to a decrease in the thiosulfate titer because copper(II) is reduced to copper(I) without liberation of iodine.

Thiocyanogen is unstable in water and decomposes in the following way:

$$3(CNS)_2 + 4H_2O \longrightarrow 5CNS^- + SO_4^{2-} + 7H^+ + HCN$$

Philip and Bramley[425] showed that the overall reaction of cupric chloride and iodide with thiocyanate is even more complicated and that, in addition to hydrocyanic acid and sulfuric acid, carbon dioxide, ammonia, urea, and dicyanogen are formed. The underconsumption of thiosulfate depends on the time of standing as well as on the iodide concentration. However, with a high enough iodide concentration, $(CNS)_2$ reacts quantitatively with iodide in aqueous solution.[426]

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[422] G. Bruhns, *Zentr. Zuckerind.*, 1917, 732; *Chem. Ztg.*, 42, 301 (1918).

[423] I. M. Kolthoff, *Pharm. Weekblad*, 55, 1338 (1918); *Chem. Ztg.*, 42, 151 (1918).

[424] D. Krüger and E. Tschirch, *Z. anal. Chem.*, 97, 161 (1934).

[425] J. C. Philip and A. Bramley, *J. Chem. Soc.*, 109, 597 (1916).

$$(CNS)_2 + 2I^- \longrightarrow 2CNS^- + I_2$$

Hence, with increasing potassium iodide concentration, the decrease in the titer of thiosulfate on standing must reach a maximum; this was proved by Krüger and Tschirch.[424] According to these authors, the decomposition of cupric thiocyanate solution in sulfuric acid in presence of iodide is explained only by the catalytic action of iodide or of intermediately formed iodine.

Kolthoff found that the following method gave good results. It is recommended that the titration be done immediately after the addition of thiocyanate.

Procedure: To the acidified copper solution add 0.5–1 ml. of *N* potassium iodide and then 10 ml. of 10 per cent potassium thiocyanate. The solution becomes dark brown because of cupric thiocyanate. Titrate with thiosulfate. The dark brown disappears and the solution assumes the brown color of iodine-iodide solution. Near the end of the titration, add 10 ml. of starch solution and titrate until the permanent change from iodine-starch blue to yellow or dirty violet. The end-point is exact to 1 drop.

Foote and Vance[427] showed that the iodometric method for the analysis of copper in ores and alloys gave excellent results if 1–2 g. of alkali thiocyanate was added near the end of the titration. To prevent the interference of iron, arsenic(V), and antimony(V), ammonium bifluoride was added to the neutral solution (about 1 g. for each 0.1 of iron). An acetate mixture (pH 3.7) can be used to buffer the solution. Their method was later improved by Oglethorpe and Smith,[428] who studied the effect of varying the ratios of thiocyanate and iodide; they showed also that an excess of iodide is not essential. Even when potassium thiocyanate was added after the iodide, low results were obtained. This was probably due to there being insufficient iodide present to convert all the cupric copper to cuprous iodide so that some cupric thiocyanate was formed and then decomposed. The end-point was not always easy to detect, the precipitate varying from a flesh color to chocolate-brown. When the time between the addition of thiocyanate and iodide was increased, correspondingly lower titers were obtained, indicating further decomposition of cupric thiocyanate. Three methods of avoiding the formation of cupric thiocyanate were examined:

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[426] H. P. Kaufmann and P. Gaertner, *Ber.*, **57**, 928 (1928).

[427] H. W. Foote and J. E. Vance, *J. Am. Chem. Soc.*, **57**, 845 (1935); *Ind. Eng. Chem., Anal. Ed.*, **9**, 205 (1937).

[428] C. C. Oglethorpe and C. G. Smith, *Analyst*, **68**, 325 (1943).

(1) *The addition of a large excess of sodium thiosulfate before the iodide and thiocyanate.* This gave improved results but only when relatively large amounts of iodide were used.

(2) *The use of a mixture of iodide and thiocyanate.* Low results could not be avoided by this means unless the amount of iodide was increased.

(3) *The addition of potassium thiocyanate toward the end of the titration.* This procedure gave excellent results and the precipitate was always almost white; 0.6 g. of potassium iodide sufficed for 25 ml. of a $0.1M$ copper solution.

Procedure: Add 0.5–0.6 g. of potassium iodide (or 5 ml. of a 10 per cent solution) to 25 ml. of the copper solution (0.05–$0.1M$). Titrate with $0.1N$ sodium thiosulfate until the brown color fades. Add a few drops of starch solution and continue the titration until the blue color first fades. Take care not to add too much thiosulfate, and ignore the reappearance of the color. Add about 1 g. of potassium or sodium thiocyanate, preferably as a 10 per cent solution; the blue color immediately intensifies. Complete the titration as quickly as possible.

Note: Haidar and Khundkar[429] determine copper and zinc in the same solution by a combination of the iodide-thiocyanate and Lang (p. 345) procedures.

From the above discussion it appears that quite a few variations of the iodometric copper titration have been proposed. An excellent review of the literature with a critical experimental study is given by Hammock and Swift.[430] They confirmed the favorable reports on the method of Foote and Vance, who add some thiocyanate before the iodine-starch end-point. The difference in consumption of thiosulfate between the thiocyanate and iodide end-points corresponds to about 0.15 ml. of $0.1N$ solution for 50 ml. of about $0.1M$ copper solution. Evidence was found by Hammock and Swift that the larger value obtained in the presence of thiocyanate is due mainly to desorption of iodine which was adsorbed by the precipitate. Apparently the thiocyanate reacts with the cuprous iodide to form cuprous thiocyanate and the adsorbed iodine is liberated.

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[429] S. Z. Haidar and M. H. Khundkar, *Anal. Chim. Acta*, **12**, 1 (1955).

[430] E. W. Hammock and E. H. Swift, *Anal. Chem.*, **21**, 975 (1949).

Procedure: To about 50 ml. of the copper solution add ammonium hydroxide or sulfuric acid to give the desired pH (see Note). Add 3 g. of iodate-free and iodine-free potassium iodide dissolved in 5 ml. of water, while swirling the solution, and titrate with thiosulfate until the brown color fades. Add 5 ml. of 0.5 per cent starch solution and titrate further until the iodine-starch color disappears. Then add 4 g. of potassium thiocyanate and titrate to the thiocyanate end-point.

Note: Hammock and Swift found that the thiocyanate can be added some 10 per cent before the end-point. The acidity can be varied greatly with sodium sulfate–sulfuric acid buffers between pH 3.15 and 0.5 without affecting the results. No interference by air-oxidation was noticed even at pH 0.5. At pH values between 1 and 2 the end-point was stable for 5–10 minutes. The titration is accurate and precise to 0.1 per cent. Chloride in amounts up to 5 g. of sodium chloride was found not to interfere.

Copper in Presence of Iron: Moser[404] complexed ferric iron with a large excess of pyrophosphate which did not react with iodide. He then added iodide and 10 ml. of glacial acetic acid and titrated after 15 minutes. Kolthoff[423] recommends for 25 ml. of iron-containing copper solution the addition of 5 g. of sodium pyrophosphate, 1.5 g. of potassium iodide, and 10 ml. of $4N$ sulfuric acid (instead of acetic acid) and then titration in the usual way.

According to Park,[412] the use of a fluoride buffer of pH 3.7 has several advantages. Under these conditions, ferric iron, pentavalent arsenic, and antimony do not interfere (see determination of copper in ores).

Kinnunen and Wennerstrand[431] have described rapid methods for the determination of copper and iron in copper-base alloys by a combination of the above procedure with that for iron (p. 343). Lead and zinc are determined by titration with ethylenediaminetetraacetic acid.

Kammori[432] has described a rapid procedure for the determination of copper in iron and steel by the Park procedure.

Copper in Presence of Arsenic: If excess sodium phosphate or sodium potassium tartrate is added to a neutral cupric solution, a clear blue solution of the complex copper compound forms which is not attacked by iodine. Thus, in a mixture of copper and arsenious acid, the arsenious oxide can be titrated with iodine after the addition of 5 g. of sodium pyrophosphate. The color change is from blue to blue-green; it should not revert after 1 minute. It is better not to use starch.

[431] J. Kinnunen and B. Wennerstrand, *Metallurgia*, 50, 149 (1954).

[432] O. Kammori, *Japan Analyst*, 2, 102, 222 (1953).

After the oxidation of trivalent arsenic, 10 ml. of 4*N* sulfuric acid and 2 g. of potassium iodide are added and the solution is titrated after 10 minutes with thiosulfate until it is bleached for 3–5 minutes. Here, of course, starch must be added. Under the given conditions, the hydrogen-ion concentration after the addition of sulfuric acid is too low to cause the reaction of arsenate with iodide. This ingenious method has been used for the analysis of Paris green.[433] Another possibility is to titrate the arsenite with bromate in hydrochloric acid solution, using methyl red indicator, and then titrate the copper iodometrically. Park[412] regulated the acidity with a biphthalate or acetate buffer solution; at a pH of less than 3.5–4, arsenate does not react with iodide within 5 minutes. Antimonic acid behaves like arsenic acid.

In the presence of metals which influence the copper titration such as Fe(III), As(V) and Sb(V), Berg[434] precipitates the copper from alkaline solution (containing about 5 per cent of sodium tartrate and 0.1–0.2*N* sodium hydroxide) with an excess of a 2 per cent solution of *o*-hydroxyquinoline (p. 551), warms to 60°C., cools, and filters. After being washed, the precipitate is dissolved in acid and titrated iodometrically in the usual way.

Verma and Singh[435] add citrate when arsenic(III) or antimony(III) is present and titrate with iodine in neutral solution. The solution is acidified to decompose the copper citrate complex, which allows the copper to be determined.

Copper in Presence of Bromate, Iodate, or Permanganate: Hume and Kolthoff[436] have worked out methods which enable copper to be determined in the presence of the above oxidizing agents; the latter are determined in the same solution.

Copper is complexed with sodium citrate and the oxidizing agent is titrated in the usual way. Mineral acid is then added to decompose the complex; the normal reaction proceeds and copper can be determined by a further titration with thiosulfate.

Iodate: To 20–50 ml. of a solution containing 0.5–3 meq. of each constituent add 2 ml. of 6*N* acetic acid and 6 g. of potassium iodide. Set aside for 3 minutes, add 20 ml. of 1.0*M* sodium citrate, and swirl until the solution becomes clear. This quantity of citrate is sufficient for 3 millimoles of copper. If the solution does not clear completely of cuprous iodide, more must be added. If more than 1 meq. of mineral acid is present in the original solution, it should be neutralized to incipient precipitation of copper hydroxide, and acetic acid added as in the regular procedure. The citrate should be tested, for some samples were found to consume iodine.

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[433] I. M. Kolthoff and C. J. Cremer, *Pharm. Weekblad*, **58**, 1620 (1921).

[434] R. Berg, *Z. anal. Chem.*, **70**, 341 (1927).

[435] M. R. Verma and Y. P. Singh, *J. Sci. Ind. Research India*, **13**, 709 (1954).

[436] D. N. Hume and I. M. Kolthoff, *Ind. Eng. Chem., Anal. Ed.*, **16**, 103 (1944); cf. P. L. Kapur and M. R. Verma, *ibid.*, **13**, 338 (1941); E. H. Swift and T. S. Lee, *ibid.*, **14**, 466 (1942).

Dilute to 200 ml. and titrate with 0.1N sodium thiosulfate, adding starch at the end-point. The color change is a sharp, easily seen transition from a deep murky blue to a clear light blue.

Copper. To the solution from the above titration add 12 ml. of 6.0N sulfuric or hydrochloric acid, wait 2 minutes, and titrate with thiosulfate.

Notes: (1) For the determination of copper, insufficient acid results in an incomplete reaction. Too large an excess causes serious air-oxidation of iodide (catalyzed by copper). Good results are obtained on adding 1 ml. of 6.0N acid for every 2 ml. of sodium citrate and then just 1 ml. in excess. It is usually advantageous to add a little more starch at the end-point. Although the citric acid present tends to sharpen the end-point somewhat, the addition of 3 g. of solid potassium thiocyanate just before the end of the titration is strongly recommended.

(2) Bromate is determined in the same way except that 6N hydrochloric acid replaces the acetic acid; 2 ml. must be added for each 30 ml. of the original sample to ensure accurate results. The amount of hydrochloric acid added for the bromate reaction must be subtracted from the amount to be added to decompose the copper complex.

(3) In a phthalate buffer of pH 5, copper reacts quantitatively with iodide without interference from bromate.

Procedure: To 20–50 ml. of the neutral sample solution add 20 ml. of a 0.1M pH 5 phthalate buffer and 3 g. of potassium iodide. Titrate with sodium thiosulfate to a starch end-point, adding 3 g. of potassium thiocyanate just before the color change. If free acid is present in the original solution, remove it by dropwise addition of ammonia until precipitation of copper hydroxide just begins.

(4) The procedure used for copper and iodate may be applied to mixtures of copper and permanganate, but sulfuric acid is used for acidification. The results are, however, 0.3–0.5 per cent low for permanganate and correspondingly high for copper. This error is due to slight oxidation of the manganous citrate complex. Accordingly it is recommended that the sum of the two substances be determined and the copper then be determined on a separate sample. This is readily accomplished by reducing the permanganate in an acid medium with saturated ferrous ammonium sulfate solution, boiling with bromine water, and then applying Park's method (p. 349), in which the effect of ferric iron is eliminated by the addition of fluoride.

Copper Determination with Excess of Thiosulfate: Copper reacts with thiosulfate according to the equation

$$2Cu^{2+} + 2S_2O_3^{2-} \longrightarrow 2Cu^{+} + S_4O_6^{2-}$$

Zecchini[437] based a determination on this reaction by adding an excess of thiosulfate, precipitating cuprous copper with ammonium thiocyanate and back-titrating with iodine. The method is not exact. Bitskei[438] improved the method considerably.

Procedure: To the neutral copper solution add 10 ml. of 20 per cent sodium potassium tartrate and 5 ml. of 20 per cent potassium thiocyanate solutions.

[437] M. Zecchini, *Staz. sper. agrar. ital.*, **32**, 17 (1899); cf. *Z. anal. Chem.*, **54**, 2521 (1915); **58**, 127 (1919).

[438] J. Bitskei, *Z. anal. Chem.*, **102**, 35 (1935); *Magyar Kem. Folyóirat*, **61**, 23 (1955).

From a small beaker add very rapidly a measured excess of 0.1N sodium thiosulfate (about 40 ml. or a 100 per cent excess). After 5 minutes, wash in the residual thiosulfate from the beaker, dilute to 80–100 ml., add 2–3 ml. of starch solution, 2 ml. of 2 per cent succinic acid solution, and titrate with 0.1N iodine solution.

Note: Thiocyanate decomposes any complex copper thiosulfate and stabilizes the cuprous ion; succinic acid prevents the interaction of iodine and thiocyanate.

Cuprous Copper: It has already been seen that the reaction between cupric ions and iodide is reversible. Under suitable conditions, if the concentration of cupric is kept very small by complexing and the iodide concentration is not too large, cuprous copper can be quantitatively titrated with iodine. Lander and Geake[439] showed that the procedure is quantitative in a bicarbonate-Rochelle salt solution. Elbs[440] worked with ammonium oxalate solutions. Several investigations have shown that the reaction is complete in solutions of oxalate, tartrate, or citrate with or without the corresponding free acid. Air is removed from the cuprous iodide suspension, citrate or oxalate is added, and the mixture is titrated rapidly with iodine. It is better to add rapidly an excess of iodine and back-titrate with thiosulfate solution. This method is suitable for the determination of copper in the presence of other oxidizing agents such as dichromate. First, the sum of all the oxidants including cupric copper is determined iodometrically in acid solution and then a suitable amount of potassium oxalate and a small excess of iodine are added. Cuprous iodide dissolves rapidly in oxalate especially in the presence of free iodine. Lang[441] reduces cupric copper to cuprous and titrates the latter iodometrically.

Reducing Sugars: The iodometric copper titration is a useful means of determining reducing sugars. When an aldose or ketose is boiled with alkaline copper solution, the cupric is reduced to cuprous copper, which precipitates as red cuprous oxide. The reaction has no simple stoichiometric equation (Vol. I, p. 251). The amount of cuprous oxide formed depends especially on the alkalinity of the solution, on the means and time of heating, on the concentration and nature of the sugar, and on the other ions present in the solution. The various sugars are all oxidized to the carboxylic acids which are immediately bound by the excess alkali. Alkali is necessary for the oxidizing action of the copper (or reducing action of the sugars), but alkali unfortunately also decomposes the sugars to other compounds which no longer possess reducing properties. Although, for example, fructose is a stronger reductant than glucose, it forms less cuprous oxide with Fehling's solution than a corresponding amount of glucose. A ketose is more easily decomposed by alkali than an aldose. If a weakly alkaline copper solution is used instead of the strongly alkaline Fehling's solution, decomposition by alkali is much less and fructose yields more cuprous oxide than glucose. A very considerable literature has developed on the iodometric determination of sugars which can only be touched upon in this book. The method is purely empirical and the values change with the conditions, as has been shown above.

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[439] G. D. Lander and J. J. Geake, *Analyst*, **39**, 116 (1914).

[440] K. Elbs, *Z. Elektrochem.*, **23**, 147 (1917).

[441] R. Lang, *Z. anorg. Chem.*, **120**, 181 (1922).

A. Use of Fehling's Solution: The Lehmann-Schoorl method[442] with Fehling's solution is commonly used. The procedure gives good results if it is adhered to exactly.[443] The cupric copper content of Fehling's solution is determined and this is repeated after boiling with the sugar solution. According to Schoorl, satisfactory results are obtained only if, after the boiling, potassium iodide is added before acidification. If the order is reversed, some of the cuprous ion is oxidized by air and low values are obtained.

Reagents: The alkaline copper solution according to Soxhlet-Meissel-Herzfeld contains solution A: 69.28 g. of crystalline copper sulfate in 1 liter; and solution B: 346 g. of Rochelle salt and 100 g. of sodium hydroxide in 1 liter.

Procedure: Pipette 10 ml. of solution A into a 200–300 ml. Erlenmeyer flask and then add 10 ml. of solution B. Add the sugar solution, generally containing less than 100 mg. of sugar, and dilute with water so that the total volume is always 50 ml. Heat the mixture over a suitable flame (the warming of the solution should take about 3 minutes) and boil for exactly 2 minutes (this time suffices for all types of sugar), during which time the flask rests on an asbestos plate with a circular hole. The solution should be only moderately boiled so that the volume is not much altered.

Cool rapidly in water to about 25°C., add 3 g. of potassium iodide dissolved in less than 10 ml. of water and then 10 ml. of 1:6 sulfuric acid, and titrate immediately with strong shaking with $0.1N$ thiosulfate solution until the iodine color returns to yellow. Add 10 ml. of starch solution and titrate slowly until the complete disappearance of the iodine starch color. The background yellow color of cuprous iodide should remain for several minutes.

Determine the empirical titer of the Fehling's solution in the same way. The solution must be boiled here because alkaline copper solution even without sugar forms a trace of cuprous oxide. For one stock solution, one determination of the titer suffices for all further determinations. The two solu-

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[442] K. B. Lehmann, *Arch. Hyg.*, **30**, 267 (1897); N. Schoorl, *Z. angew. Chem.*, **12** 633 (1899); *Z. anal. Chem.*, **56**, 191 (1917).

[443] E. Rupp and F. Lehmann, *Apoth. Ztg.*, **24**, 73 (1909); *Arch. Pharm.*, **247**, 516 (1910); B. Nordhoff, *Apoth. Ztg.*, **27**, 8 (1912); W. Griesbach and H. Straszner, *Z. physiol. Chem.*, **88**, 198 (1913); G. Bruhns, *Zentr. Zuckerind.*, **25**, 51 (1917).

TABLE I

Sugar Reduction Table According to Schoorl

Reduced copper (ml. 0.1N solution)	Glucose (mg.), $C_6H_{12}O_6$	Δ	Fructose (mg.), $C_6H_{12}O_6$	Δ	Invert sugar (mg.), $C_6H_{12}O_6$	Δ	Saccharose (mg.), $C_{12}H_{22}O_{11}$	Δ	Lactose (mg.), $C_{12}H_{22}O_{11}$ H_2O	Δ	Maltose (mg.), $C_{12}H_{22}O_{11}$	Δ	Galactose (mg.), $C_6H_{12}O_6$	Δ	Mannose (mg.), $C_6H_{12}O_6$	Δ	Arabinose (mg.), $C_5H_{10}O_5$	Δ	Xylose (mg.), $C_5H_{10}O_5$	Δ	Rhamnose (mg.), $C_6H_{12}O_5$	Δ
1	3,2	3,1	3,2	3,2	3,2	3,2	3,1	3,1	4,6	4,6	5,0	5,5	3,3	3,4	3,1	3,2	3,0	3,0	3,1	3,2	3,2	3,3
2	6,3	3,1	6,4	3,3	6,4	3,3	6,2	3,1	9,2	4,7	10,5	5,5	7,0	3,4	6,3	3,2	6,0	3,1	6,3	3,2	6.5	3,4
3	9,4	3,2	9,7	3,3	9,7	3,3	9,3	3,1	13,9	4,7	16,0	5,5	10.4	3,6	9,5	3,3	9.2	3,3	9,5	3,3	9,9	3,4
4	12.6	3,3	13,0	3,4	13,0	3,4	12,4	3,2	18,6	4,7	21,5	5,5	14,0	3,5	12,8	3,3	12,3	3,2	12,8	3,3	13,3	3,5
5	15,9	3,3	16,4	3,6	16,4	3,4	15,6	3,2	23,3	4,8	27,0	5,5	17.5	3,6	16,1	3,3	15.5	3,2	16.1	3,3	16,8	3,4
6	19.2	3,2	20.0	3,7	19,8	3,4	18,8	3,2	28.1	4,9	32.5	5,5	21.1	3,6	19,4	3,4	18,7	3,2	19,4	3,4	20.2	3,5
7	22,4	3,2	23,7	3,7	23,2	3,3	22.0	3,2	33,0	5,0	38,0	5,5	24,7	3,6	22,8	3,4	21,9	3,3	22,8	3,4	23,7	3,5
8	25,6	3,3	27,4	3,7	26,5	3,4	25,2	3,2	38.0	5,0	43,5	5,5	28,3	3,7	26,2	3,4	25,2	3,4	26,2	3,4	27,2	3,6
9	28.9	3,4	31.1	3,8	29,9	3,5	28,4	3,3	43,0	5,0	49,0	6	32.0	3,7	29,6	3,4	28,6	3,4	29,6	3,4	30,8	3,6
10	32.3	3,4	34.9	3,8	33,4	3,4	31,7	3,3	48,0	5,0	55,0	5,5	35,7	3,7	33,0	3,5	32,0	3,4	33,0	3,5	34,4	3,6
11	35,7	3,3	38,7	3,7	36,8	3,5	35,0	3,3	53,0	5,0	60,5	5,5	39,4	3,7	36,5	3,5	35,4	3,4	36,5	3,5	38,0	3,6
12	39.0	3,4	42.4	3,8	40,3	3,5	38,3	3,3	58,0	5,0	66,0	6	43,1	3,7	40,0	3,5	38,8	3,4	40,0	3,5	41,6	3,6
13	42.4	3,4	46.2	3,8	43,8	3,5	41.6	3,3	63,0	5,0	72,0	6	46,8	3,7	43,5	3,5	42.2	3,4	43,5	3,5	45,2	3,6
14	45,8	3,5	50,0	3,7	47,3	3,5	44,9	3,3	68,0	5,0	78,0	5,5	50,5	3,8	47,0	3,6	45,6	3,4	47,0	3,6	48,8	3,6
15	49,3	3,5	53,7	3,8	50,8	3,5	48,2	3,4	73,0	5,0	83,5	5,5	54,3	3,8	50,6	3,6	49,0	3,4	50.6	3,6	52,4	3,6
16	52,8	3,5	57.5	3,7	54,3	3,7	51,6	3,5	78,0	5,0	89,0	6	58,1	3,8	54.2	3,7	52,4	3,4	54.2	3,7	56,0	3,8
17	56,3	3,5	61,2	3,8	58,0	3,8	55,1	3,6	83,0	5,0	95,0	6	61,9	3,8	57,9	3,7	55,8	3,5	57,9	3,7	59,8	3,7
18	59,8	3,5	65,0	3,7	61,8	3,7	58,7	3,6	88,0	5,0	101,0	6	65,7	3,9	62,6	3,7	59,3	3,6	62,6	3,7	63,5	3,8
19	63.3	3,6	68,7	3,7	65,5	3,9	62,3	3,6	93,0	5,0	107.0	5,5	69,6	3,8	65,3	3,9	62,9	3,6	65,3	3,9	67,3	3,7
20	66,9	3,8	72,4	3,8	69,4	3,9	65,9	3,7	98,0	5,0	112,5	6	73,4	3,8	69,2	3,9	66,5	3,7	69,2	3,9	71,0	3,8
21	70,7	3,8	76,2	3,9	73,3	3,9	69,6	3,7	103,0	5,0	118,5	6	77,2	4,0	73,1	3,9	70,2	3,8	73,1	3,9	74,8	3,8
22	74.5	4,0	80.1	3,9	77,2	4,0	73,3	3,8	108,0	5,0	124,5	6	81,2	3,9	77,0	4,0	74,0	3,9	77,0	4,0	78,6	3,8
23	78.5	4,1	84,0	3,8	81,2	4,0	77,1	3,8	113,0	5,0	130,5	6	85,1	3,9	81,0	4,0	77,9	3,9	81,0	4,0	82,4	3,8
24	82,6	4,0	87,8	3,9	85,2	4,0	80,9	3,8	118,0	5,0	136,5	6	89,0	4,0	85,0	4,0	81,8	3,9	85,0	4,0	86.2	3,8
25	86,6		91.7		89,2		84,7		123,0		142,5		93,0		89,0		85,7		89,0		90,0	

tions are kept separate because the mixture gradually decomposes to form cuprous oxide. The difference between the blank determination and the titer found in the analysis corresponds to the copper reduced by the sugar. The amount of sugar present can be found in Table I.

Notes: (1) The figure given for saccharose is naturally that of invert cane sugar. The inversion is most easily carried out by the method of von Fellenberg:[444] dissolve 5 g. of cane sugar in 50 ml. of 0.02*N* hydrochloric acid and heat for half an hour on a boiling water bath. Cool, neutralize to methyl orange with 1 ml. of *N* sodium hydroxide, and dilute with water to 500 ml.

(2) Alternatively, the cuprous oxide formed can be determined. Filter on a sintered-glass crucible, wash, dissolve in neutral ferric alum solution, and titrate with permanganate (p. 88) or dichromate in the presence of phosphoric acid, using diphenylamine as indicator (p. 179). With the help of Table I the consumption can be directly converted to the sugar content. When only small amounts of sugar are present, this direct method is advantageous.

(3) In contrast to larger amounts of uninverted saccharose, the reduction value of the oxidizable varieties of sugar alters a little. Saccharose has but a small reducing power. For details, the papers of Schoorl[445] and, especially, Bruhns[446] should be consulted.

(4) Calcium salts interfere with the determination (especially that of lactose); too little copper is reduced.

Titration of Copper according to Bruhns: For the iodometric determination of cupric copper it has already been seen (p. 351) that a large addition of potassium iodide is unnecessary if much potassium thiocyanate is used. This can also be used in sugar analysis.

Procedure:[446] After the reduction, mix the cooled solution with 5 ml. of iodide-thiocyanate solution (containing 0.67 g. of KCNS and 0.1 g. of KI). Add rapidly with swirling 10 ml. of 6*N* hydrochloric acid and titrate immediately with thiosulfate until the brown color turns to grey. Then add 10 ml. of 0.2 per cent starch solution and titrate further until the precipitate appears yellow and does not revert to blue or grey after 5 minutes. Schoorl and Kolthoff[447] found it better to add 1 ml. of *N* potassium iodide to the cooled solution. Two flasks are prepared containing 10 ml. of 6*N* hydrochloric acid and 20 ml. of 20 per cent potassium thiocyanate. The acid is added all at once followed by rapid shaking and immediate addition of thiocyanate and titration with thiosulfate. The rapid series of additions is essential to avoid air-oxidation of cuprous copper.

Iodometric Determination of the Cuprous Oxide Formed: Several procedures based on this principle have been described.[448] Kolthoff[449] developed a method in which the amount of sugar could be derived from the Schoorl table (Table I). Since the cuprous oxide formed is determined, the copper solution need not be exactly measured.

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[444] T. von Fellenberg, *Mitt. Gebiete Lebensm. u. Hyg.*, 11, 148 (1920).

[445] N. Schoorl, *Chem. Weekblad*, 9, 678 (1912).

[446] G. Bruhns, *Zentr. Zuckerind.*, 27, 621 (1919).

[447] N. Schoorl and I. M. Kolthoff, *Pharm. Weekblad*, 54, 959 (1917); 55, 1338 (1918).

Procedure: After boiling and cooling (p. 358), add 20 ml. of approximately *M* sodium carbonate, 25 ml. of 0.1*N* potassium iodate, and 20 ml. of 4*N* hydrochloric acid. Dissolve the cuprous oxide by shaking. Add 4 ml. of *N* potassium iodide and, after 1 minute, 20 ml. of 10 per cent potassium oxalate. Titrate the iodine with thiosulfate, using starch indicator. The difference in consumption from a blank value gives the amount of cuprous oxide formed.

Notes: (1) For the blank determination add 5 ml. of potassium iodide and wait 2 minutes before adding oxalate. The cuprous oxide can also be directly titrated. After cooling, add no iodate but acidify, mix with oxalate, and titrate directly with thiosulfate, using starch indicator.

(2) The direct titration of cuprous oxide after sugar reduction is unsatisfactory because of air-oxidation. It is necessary to add sodium carbonate, which provides an atmosphere of carbon dioxide after acidification.

(3) The amount of hydrochloric acid added must be measured fairly carefully; it corresponds to the alkalinity of the Fehling's solution.

(4) After the addition of iodide, 1–2 minutes are allowed for quantitative reaction between iodate and iodide.

(5) Near the end of the titration, the brownish color becomes almost green. Starch is then added and the titration continued until the change is from dark to clear blue. The end-point is very exact, and the deep blue color does not return even after long standing. The method is somewhat inconvenient in that so many reagents are required.

B. Modified Method with the Reagent of Stanley-Benedikt:[450] The reagent is a solution of copper citrate which is made alkaline with sodium carbonate, the alkalinity being much less than that Fehling's solution. It oxidizes the different kinds of sugar more slowly than Fehling's solution; for the most complete possible oxidation[451] it is necessary to boil for exactly 10 minutes and to use a reflux condenser to avoid excessive loss of water. The Stanley-Benedikt reagent has a considerable advantage over Fehling's solution in that the warming of the solution plays a secondary role; it should be heated to boiling over a free flame within 2 minutes. Glucose and fructose give the same reduction values for a boiling time of 10 minutes.

Reagent: 0.1*M* in copper sulfate and 1*M* in sodium carbonate: 25 g. of copper sulfate (iron-free) in 100 ml. of water; 50 g. of citric acid ($C_6H_8O_7 \cdot H_2O$) in 50 ml.

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[448] F. M. Scales, *J. Biol. Chem.*, **23**, 81 (1915); *Ind. Eng. Chem.*, **11**, 747 (1919); T. von Fellenberg, *Mitt. Gebiete Lebensmitt. u. Hyg.*, 11, 129 (1920); P. A. Shaffer and A. F. Hartmann, *J. Biol. Chem.*, **45**, 349 (1920); M. Somogyi, *J. Biol. Chem.*, **160**, 61, 69 (1945).

[449] I. M. Kolthoff, *Arch. Suikerind. Ned. Indië*, **1926**, 124.

[450] N. Schoorl, *Chem. Weekblad*, **26**, 130 (1929).

[451] Cf. N. Schoorl, *Chem. Weekblad*, **9**, 706 (1912).

of water; 388 g. of sodium carbonate decahydrate (or a corresponding amount of the anhydrous salt) in 300–400 ml. of warm water. Pour the citric acid solution into the carbonate and add the copper sulfate. Dilute with water to 1 liter. After the solution has been allowed to stand for some days, filter or siphon off from the deposit.

The correct alkalinity of the solution is very important and, because crystalline soda effloresces easily, a determination using dimethyl yellow is necessary. Alternatively the alkalinity of the prepared reagent can be controlled by diluting 10 ml. to 100 ml. with water, acidifying 10 ml. of this solution with 25 ml. of 0.1*N* hydrochloric acid, boiling off carbon dioxide, and back-titrating to phenolphthalein. Six milliliters of 0.1*N* sodium hydroxide should be required (not 5 ml. as would be expected because the copper is not completely bound in the complex).

Procedure: To an Erlenmeyer flask of Pyrex or Jena glass add 25 ml. of the copper solution and the measured sugar solution. Dilute to a total volume of 50 ml. with water. Add some boiling stones and heat over a free flame to boiling in 2 minutes. Insert a reflux condenser and boil for 10 minutes over a wire gauze. Cool rapidly in water and, after another 5 minutes, determine the unconsumed cupric copper or the cuprous oxide formed. Find the amount of sugar from Table II.

(*a*) *Back-Titration of Copper:* To the cold solution add 3 g. of potassium iodide and 25 ml. of 25 per cent sulfuric acid (carefully) and titrate with

TABLE II

Sugar Reduction Table According to Schoorl with Stanley-Benedikt Solution

Ml. 0.1 *N* thio	Glucose, fructose or invert sugar, $C_6H_{12}O_6$ mg.	Δ	Lactose, $C_{12}H_{22}O_{11}$ mg.	Δ	Maltose, $C_{12}H_{22}O_{11}$ mg.	Δ
1	2.4	2.4	3.6	3.7	3.9	3.9
2	4.8	2.4	7.3	3.7	7.8	3.9
3	7.2	2.5	11.0	3.7	11.7	3.9
4	9.7	2 5	14.7	3.7	15.6	4.0
5	12.2	2.5	18.4	3.7	19.6	3.9
6	14 7	2 5	22.1	3.7	23.5	4.0
7	17.2	2.6	25.8	3.7	27.5	4.0
8	19.8	2.6	29.5	3.7	31.5	4.0
9	22.4	2.6	33.2	3.8	35.5	4.0
10	25.0	2 6	37.0	3.8	39.5	4.0
11	27.6	2.7	40.8	3.8	43.5	4.0
12	30.3	2.7	44.6	3.8	47.5	4.1
13	33.0	2.7	48.4	3.8	51.6	4.1
14	35.7	2 8	52.2	3.8	55.7	4.1
15	38.5	2 8	56.0	3.9	59.8	4.1
16	41.3	2.9	59.9	3.9	63.9	4.1
17	44.2	2.9	63.8	3.9	68.0	4.2
18	47.1	2.9	67.7	4.0	72.2	4.3
19	50.0	3.0	71.7	4.0	75.5	4.4
20	53.0	3.0	75.7	4.1	80.9	4.5
21	56.0	3.1	79.8	4.1	85.4	4.6
22	59.1	3.1	83.9	4.1	90.0	4.6
23	62.2		88.0		94.6	

0.1*N* thiosulfate. Alternatively, add 3 ml. of *N* potassium iodide and, rapidly but carefully, 20 ml. of 25 per cent hydrochloric acid followed by 10 ml. of 20 per cent potassium thiocyanate. Titrate with thiosulfate after strong shaking.

(*b*) *Determination of Cuprous Oxide Formed:* To the cold solution add about 50 ml. of 0.4*N* acetic acid (pH neutralized to about 8), shake, add 25 ml. of 0.1*N* iodine (exactly measured), shake again, and add carefully 55 ml. of 0.75*N* hydrochloric acid. Shake to dissolve all the oxide and back-titrate with 0.1*N* thiosulfate, adding starch near the end-point and titrating further to the change to clear blue.

Note: As with the Fehling's solution method, other salts have a marked influence on the result. On boiling 50 mg. of glucose in the presence of 1 millimole of the following salts, Schoorl found the following values instead of 19 ml. of 0.1*N* thiosulfate:

	NaCl	NH_4Cl	CaCl	MgSO	ZnSO
	18.90	19.25	18.80	19.30	19.90
Correction:	+0.10	−0.25	+0.20	−0.30	−0.90

A useful survey of available methods for estimating reducing sugars has been given by McDonald.[452] This may allow some choice to be made to suit a particular set of circumstances. Possibly the best of the more recent critical discussions and surveys is the paper by Blom and Rosted.[453] They examined iodine, ferricyanide, and copper tartrate methods and developed a new method which uses potassium copper carbonate as reagent. This method has the advantage that only inorganic salts (which can be obtained in a high state of purity) are required for preparing the reagent; the reagent has a well-defined pH and a very high buffer capacity. The relative uncertainty of a single determination is 0.8 per cent. The reagent is not, however, without defects; it cannot be prepared more concentrated than about 0.17*M* with respect to copper, and the solution cannot be diluted substantially without the copper complex hydrolyzing. The boiling time of 45 minutes which is necessary is an inconvenience for a single analysis.

Reagents: (1) Dissolve 41.6 g. of copper sulfate pentahydrate in 200 ml. of boiling water contained in a 1 liter beaker. Cool and add cautiously 23 g. of potassium carbonate while stirring. When carbon dioxide has escaped add 400 ml. of water, 166.9 g. of powdered potassium bicarbonate, and 230.3 g. of potassium carbonate. When most of the salts have dissolved, wash the total contents of the beaker into a 1 liter graduated flask, dilute to the mark with water, and mix thoroughly. Set aside and leave overnight to allow potassium sulfate to settle out; filter this off. The solution is not stable indefinitely.

(2) Dissolve 33.2 g. of potassium iodide and 1 g. of sodium carbonate (stabilizer) in water and dilute to 1 liter.

(3) Dissolve 1 g. of lead acetate in 20 ml. of water containing 4–5 drops of

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[452] E. J. McDonald, *Principles of Sugar Technology*, P. Honig, ed., Elsevier, 1953, p. 104.

[453] J. Blom and C. O. Rosted, *Acta Chem. Scand.*, 1, 32 (1947).

glacial acetic acid. Add 333 ml. of concentrated hydrochloric acid and dilute to 1 liter.

Procedure: Weigh or pipette the sugar solution (less than 10 ml.) into a 25 ml. graduated flask (marked with weight in decigrams, width of neck 8–9 mm., surface about 0.6 sq. cm., and equipped with numbered rings). Add 15 ml. of copper reagent. Pipette 15 ml. of the reagent into 2 or 3 similar flasks for blank determinations. Fill the flasks to the mark, shake, and place in a boiling water bath, the level of which is kept above the graduation marks of the flasks. The water must not cease boiling and splashing must be avoided throughout this operation. Note the time. After 45 minutes cool the flasks in running water. Measure 5 ml. lots of the iodide solution into 300 ml. Erlenmeyer flasks, transfer the reaction mixture to these flasks, and rinse the graduated flasks three times with distilled water. Ignore any deposited cuprous oxide. Dissolve the ring of cupric oxide, which is often found on the neck of the flasks used for blank determinations, with a few milliliters of the lead acetate solution and wash into the titration flask. Add 25 ml. of lead solution carefully. Shake while carbon dioxide escapes and then add 5 ml. of a solution containing 194 g. of potassium thiocyanate per liter. Titrate immediately with $0.1M$ sodium thiosulfate and near the end-point add a 2 per cent solution of soluble starch (previously centrifuged to remove particles which obscure the end-point). The color change is from blue to white-yellow for small amounts of cupric copper and from blue to pink for larger amounts.

Note: The effect of atmospheric oxygen is minimized by the narrow necks of the flasks. The numbered rings are presumably for identification purposes.

Polyvalent Alcohols: The copper titration has a further application in the determination of polyvalent alcohols. The determination of glycerin (glycerol) was described by Wagenaar[454] whose method was improved by Kolthoff and Beckers.[455] A similar method has been used for mannitol.[456] These methods have only slight practical importance, for they are purely empirical and the amount of dissolved copper depends strongly on the alkalinity of the solution and on other factors.

Glycerol: Bertram and Rutgers[457] found that under certain conditions 1 mole of glycerol dissolved 1 mole of copper oxide. Schoorl[458] investigated their procedure and found reasonably good results with quantities of glycerol of the order of 250–400 mg. Schoorl recommends the following procedure.

Procedure: Introduce into a 100 ml. volumetric flask a known weight (not more than 10 ml.) of the glycerol solution which should contain less than 500 mg.

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[454] M. Wagenaar, *Pharm. Weekblad*, **48**, 497 (1911).

[455] I. M. Kolthoff and J. H. M. Beckers, *Pharm. Weekblad*, **55**, 272 (1918).

[456] J. Smit, *Chem. Weekblad*, **41**, 894 (1913).

[457] S. H. Bertram and H. Rutgers, *Rec. trav. chim.*, **57**, 681 (1938).

[458] N. Schoorl, *Pharm. Weekblad*, **76**, 777 (1939).

of glycerol. Dilute to 10 ml. with water, add 10 ml. of 7.5*N* sodium hydroxide (30 g. in 100 ml.), and 60 ml. of 96 per cent alcohol, mix and slowly add from a burette with constant stirring a 10 per cent solution of copper chloride dihydrate in alcohol until the precipitate of copper hydroxide no longer dissolves. Then add an equal volume of the copper chloride solution, cool to room temperature, and dilute to the mark with alcohol. Mix thoroughly and centrifuge the suspension or allow to stand overnight. Determine the copper content of the centrifugate or the clear supernate, after boiling off the alcohol, by the addition of 8–10 ml. of 4*N* sulfuric acid and 1 g. of potassium iodide and titration with 0.1*N* thiosulfate, using starch as indicator. One milliliter of 0.1*N* thiosulfate corresponds to 9.2 mg. of glycerol.

Note: Cane sugar under these conditions yields a very insoluble copper compound. Reducing sugars must be oxidized before centrifuging. Mannitol and sorbitol (1 mole dissolves 2 atoms of copper) and tartrate (1 mole dissolves 1 atom of copper) can be determined in the above way using aqueous instead of alcoholic solutions.

18. Cobalt. In slightly alkaline solution cobalt oxide is easily converted to the higher oxidation state, Co_2O_3. After the oxidation material has been removed, the sesquioxide can be titrated in several ways. A review of the early literature has been given by Willard and Hall,[459] who tested different methods and recommended that of Engle and Gustavson.[460]

Procedure: Neutralize the cobalt solution approximately and add 1 g. of sodium perborate and 3 g. of sodium hydroxide. Boil the mixture for 10 minutes in a flask with a ground-glass stopper and cool while carbon dioxide passes through to keep out air. Add 2 g. of potassium iodide, acidify with 100 ml. of 20 per cent sulfuric acid, and allow the closed flask to stand until all the precipitate has dissolved. Titrate with 0.25*N* thiosulfate.

$$2Co(OH)_3 + 6KI \longrightarrow 2CoI_2 + H_2O + I_2$$

Notes: (1) Cobalt sesquioxide dissolves only slowly in the acid iodide solution so that air must be excluded to prevent atmospheric oxidation of hydriodic acid.[459]

(2) Nickel does not interfere. Oxidation is incomplete when more than 7 mg. of iron is present. Ferric iron is quantitatively reduced by hydriodic acid and is also titrated. Details are given by Willard and Hall. If the cobalt is to be determined in presence of varying amounts of iron, it can be precipitated with phenylthiohydantoic acid.[461] The precipitate is treated with concentrated hydrochloric and nitric acids to decompose the organic material, treated further with sulfuric acid and, after evaporation, the cobalt is determined as above. It is simpler to dry the precipitate, ash, decompose with potassium pyrosulfate, dissolve in water, neutralize, etc.

(3) The cobalt sesquioxide can be reduced with reductants other than hydriodic acid. Willard and Hall obtained excellent results with a strong acid solution of stannous chloride, with careful exclusion of air. The excess of stannous ion can be titrated with iodine (p. 319), iodate (p. 459), bromate (p. 517), or dichromate (p. 196). The original paper should be consulted for details.[459]

(4) Willard and Hall[461] used this cobalt method for the analysis of steels.

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[459] H. H. Willard and D. Hall, *J. Am. Chem. Soc.*, **44**, 2237 (1922).

[460] W. D. Engle and R. G. Gustavson, *Ind. Eng. Chem.*, **8**, 901 (1916).

[461] H. H. Willard and D. Hall, *J. Am. Chem. Soc.*, **44**, 2221 (1922).

Treat about 0.7 g. of steel with hydrochloric acid (sp. gr. 1.1). Tungsten separates as a black powder. Add 1–2 ml. of 85 per cent phosphoric acid and 3 ml. of nitric acid slowly and warm the mixture until all is in solution. Add 7 g. of citric acid and ammonia until the solution is alkaline, then add 6 ml. in excess. To the warm alkaline solution add a solution of 1 g. of phenylthiohydantoic acid in 30 ml. of hot water with constant stirring. Dry the precipitate, ash, and continue as in Note 2.

(5) Malaprade[462] examined the Job method[463] in which cobalt in bicarbonate solution is oxidized by hydrogen peroxide; but he preferred the oxidation in strong alkaline medium.

Procedure: To 100 ml. of neutral solution add 20–30 ml. of hydrogen peroxide solution and 3 g. of sodium or potassium hydroxide dissolved in a little water. Hydrated cobaltic oxide precipitates and catalyzes the decomposition of the hydrogen peroxide. Boil the solution for 2 minutes to complete the removal of oxidant. Cool, add 4–5 g. of potassium iodide, acidify with sulfuric or hydrochloric acid, and, after complete dissolution of the cobalt precipitate, titrate in the usual way with thiosulfate. The precipitate dissolves only slowly.

Nickel, manganese, iron, anions which complex cobalt (e.g., pyrophosphate), and ammonia interfere. The method of Willard and Hall is much more widely applicable.

Laitinen and Burdett[464] determined cobalt in complex compounds by igniting to the oxide and fusing this with pyrosulfate. The solution is treated with potassium bicarbonate and hydrogen peroxide to form a carbonate complex of cobalt(III) which reacts with iodide after the addition of excess of acid.

Procedure: To 20–25 ml. of solution in a 250–300 ml. Erlenmeyer flask containing 1.5–250 mg. of cobalt in sulfuric acid solution add sufficient sodium or potassium bicarbonate to neutralize the acid, then add 5 g. in excess. Add 5 ml. of 30 per cent hydrogen peroxide and, after effervescence has subsided somewhat, rinse the sides of the flask with distilled water to ensure complete oxidation of the cobalt. This also serves to wash down any hydrogen peroxide which was spattered on the walls of the flask by the effervescing solution, in order to allow it to undergo decomposition.

Heat the solution gently until the effervescence due to the decomposition of the hydrogen peroxide ceases. (If the cobalt concentration is $0.5M$ or higher, standing at room temperature for 5 minutes will destroy the excess hydrogen peroxide. If the solution is heated too long or too strongly, some decomposition of the complex may occur.) Add several small portions (0.5 g.) of potassium (or sodium) bicarbonate at intervals during the heating period. (This step has proved effective in keeping the complex stable.)

Cool the solution in an ice water bath, dilute to 100 ml., and add 5 g. of potassium iodide. Carefully neutralize the solution with 1:1 hydrochloric acid, adding the acid dropwise while swirling the solution until the effervescence ceases, then add 10 ml. in excess and titrate the liberated iodine with standard thiosulfate solution.

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[462] L. Malaprade, *Bull. soc. chim., France,* (4) **47**, 405 (1930).

[463] A. Job, *Ann. chim. et phys.*, (7) **20**, 205 (1900).

[464] H. A. Laitinen and L. W. Burdett, *Anal. Chem.*, **23**, 1268 (1951).

Notes: (1) When very dilute (e.g., $0.001M$) thiosulfate solutions are used, an amperometric titration is recommended, especially if iron is present.[464]

(2) Iron, chromium, manganese, copper, antimony, molybdenum, vanadium, and tungsten interfere. The interference of iron can be largely prevented by adding 2 g. of sodium or potassium fluoride and 2 g. of sodium acetate before the addition of bicarbonate, and filtering off the precipitate through a medium sintered-glass crucible. Nickel also interferes.

(3) Yalman[465] has recently described a method based on the formation of iodopentammine cobalt(III) nitrate, the excess of the iodine used in the formation of the complex being titrated with standard arsenite. Satisfactory results were obtained only when a potentiometric titration was used; with starch as indicator the end-points were unsatisfactory and, when large amounts of cobalt were present, it was necessary to filter off the precipitate.

(4) Methods for the determination of cobalt and nickel have been described in which they are oxidized to the trivalent state with persulfate and are then titrated iodometrically.[466]

19. Cerium. Trivalent cerium can be oxidized by various materials to the quadrivalent form, which has strong oxidizing properties and is quantitatively reconverted to trivalent form by reductants such as hydriodic acid or ferrous salts.

$$2Ce^{4+} + 2I^- \longrightarrow 2Ce^{3+} + I_2$$

Von Knorre[467] investigated the reaction and used persulfate as oxidant. Metzger[468] used sodium bismuthate. Willard and Young[469] systematically examined the conditions for the complete oxidation of cerium by persulfate. Small amounts of silver salts are good catalysts for the oxidation.

Procedure:[469] To 25 ml. of cerous solution in N sulfuric acid add 2.5–10 ml. of concentrated sulfuric acid (sp. gr. 1.83), dilute to 200 ml. with water, and add 1–1.5 g. of ammonium persulfate and 2–5 ml. of 0.25 per cent silver nitrate. Boil the mixture for 10 minutes, after which time the excess of persulfate has decomposed, cool, add 1–2 g. of potassium iodide, and titrate with thiosulfate.

Notes: (1) The ceric salt can also be determined by other reductants, e.g., ferrous sulfate. Add excess of standard ferrous solution and back-titrate with dichromate (p. 177) or ceric sulfate (p. 147).

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[465] R. G. Yalman, *Anal. Chem.*, **28**, 91 (1956).

[466] L. Dede and H. Zieriacks, *Z. anal. Chem.*, **124**, 25 (1942); cf. E. S. Tomula, O. Juntinen, and P. Tanksanen, *ibid.*, **135**, 265 (1952).

[467] G. von Knorre, *Z. angew. Chem.*, **11**, 717 (1897).

[468] F. J. Metzger, *J. Am. Chem. Soc.*, **31**, 523 (1909).

[469] H. H. Willard and P. Young, *ibid.*, **50**, 1379 (1928); cf. N. H. Furman, *ibid.*, 761.

(2) The air-oxidation of hydriodic acid causes an error in the titration of the liberated iodine, according to Furman and Wallace.[470]

(3) An interesting procedure has been described by Přibil *et al.*[471] which enables chromate, permanganate, or cerium(IV) to be determined in the presence of ferric iron and copper(II). After all the oxidizing ions present have been reduced with iodide, EDTA is added and in its presence the ferrous and cuprous ions are immediately oxidized by the iodine liberated in the first reaction. Stable ferric and cupric complexes are formed with EDTA. The residual iodine is equivalent to the chromate, permanganate, or cerium(IV) ions originally present. Sodium acetate (to maintain the solution at the optimum pH of 4–5), excess of EDTA and potassium iodide are added. The remaining iodine is titrated after 5 minutes with 0.1*N* thiosulfate. Ferrous and cuprous ions are very sensitive to air-oxidation in presence of EDTA, but presumably iodine oxidation takes place preferentially.

20. Gold. Herschlag[472] gives the following procedure for the determination of gold which is a modification of the method proposed by Pollard.[473] The determination is based on the reaction

$$AuCl_3 + 3KI \longrightarrow AuI + I_2 + 3KCl$$

Procedure: To the sample containing about 40 mg. of gold in a volume of 20 ml. or less add 15 ml. of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid and heat briefly in a hood. Remove the flame and add 25 ml. of 5 per cent sodium hypochlorite solution. Add 35 ml. of distilled water and boil gently for 10 minutes. Cool, neutralize the acid with a saturated solution of sodium carbonate or with sodium hydroxide testing the reaction with litmus paper. Adjust to slightly acid with hydrochloric acid and add a saturated solution of sodium bicarbonate until the solution is alkaline to litmus paper. Add quickly while stirring a solution of 2–3 g. of potassium iodide in a little water and titrate the iodine with 0.01*N* arsenic trioxide solution until the blue color of the starch has disappeared.

Notes: (1) Copper, iron, and other base metals do not interfere. Platinum and palladium do not cause liberation of iodine, but they form strongly colored iodide complexes which make the end-point difficult to determine.

(2) A micro method has been described by Lespagnol and Merville.[474] The aqueous solution containing 2–3 mg. of gold is transferred to a centrifuge tube and treated with 2 ml. of a 40 per cent formaldehyde solution and 0.5 ml. of a sodium hydroxide solution. After 15 minutes on the steam bath, the surface of the liquid is dusted with talc and the metallic gold is centrifuged and washed with water in the tube. To the metallic gold are added 1 ml. of concentrated hydrochloric acid, 2 ml. of standard 0.1*N* iodine solution, and 1 ml. of 5 per cent sodium iodide. The mixture is stirred until the gold dissolves and is then back-titrated with 0.1*N* thiosulfate solution from a microburette. A blank is run on the reagents. The gold is said to form gold iodide on treatment with iodine. The procedure is applicable to medicinal preparations.

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[470] N. H. Furman and J. H. Wallace, *J. Am. Chem. Soc.*, **53**, 1283 (1931); see also R. Bunsen, *Ann.*, **105**, 40 (1858); P. E. Browning, *Z. anorg. Chem.*, **22**, 297 (1900); J. Martin, *J. Am. Chem. Soc.*, **49**, 2133 (1927).

[471] R. Přibil, V. Simon, and J. Doležal, *Collection Czech Chem. Communs.*, **16–17**, 573 (1951–2).

[472] V. E. Herschlag, *Ind. Eng. Chem., Anal. Ed.*, **13**, 561 (1941).

[473] W. B. Pollard, *Bull. Inst. Mining Met.*, **Nos. 330–1**, 23 (1932).

[474] A. Lespagnol and R. Merville, *Bull. soc. pharm. Lille*, **1945**, 48.

21. Mercury. ***Mercurous Salts:*** Mercurous salts are converted by iodine–potassium iodide solution into the strong complex compound potassium mercury iodide:

$$Hg_2Cl_2 + I_2 + 6I^- \longrightarrow 2HgI_4^{2-} + 2Cl^-$$

On this basis, Hempel[475] proposed a method for the determination of calomel.

Procedure: To about 240 mg. of calomel in a glass-stoppered Erlenmeyer flask add 25 ml. of 0.1*N* iodine and 1 g. of potassium iodide. Shake until the precipitate dissolves. Back-titrate with 0.1*N* thiosulfate. One milliliter of 0.1*N* iodine corresponds to 11.8 mg. of mercurous chloride.

Note: Iodine may be prepared *in situ* from 0.1*N* iodate or bromate solution with excess of iodide and acid.

Mercuric Salts: Mercury is precipitated as the metal in alkaline solutions. It is then oxidized by excess of 0.1*N* iodine, which is then back-titrated.

$$Hg + I_2 + 2I^- \longrightarrow HgI_4^{2-}$$

The method is of practical value in the determination of sublimate in which mercury cannot be determined with thiocyanate by the Volhard method (Vol. II, p. 336).

Procedure:[476] Transfer a suitable amount of the sublimate solution containing about 200 mg. of mercuric chloride to a glass-stoppered flask and add 1–2 g. of potassium iodide so that the mercury iodide originally precipitated redissolves. Make the solution alkaline with 10 ml. of 4*N* sodium hydroxide and add with strong shaking a mixture of about 3 ml. of pure, approximately 35 per cent formaldehyde solution and 10 ml. of water. Shake for about 2 minutes, acidify with 10 ml. of acetic acid, shake again thoroughly, and finally add 25 ml. of 0.1*N* iodine or iodate solution. Shake again until all the mercury has dissolved and titrate the excess of oxidant with 0.1*N* thiosulfate. One milliliter of 0.1*N* iodine corresponds to 13.75 mg. of mercuric chloride.

Notes: (1) Fleury and Marque[477] observed that finely divided mercury dissolved quickly in iodine solution. Before the reduction in alkaline solution, they added 10 ml. of approximately 10 per cent barium sulfate suspension.

Fitzgibbon[478] found that mercury dissolved more rapidly when gelatin was present as a protective colloid. He used the above method but warmed the solution to 60°C. after the addition of alkali and added 2 ml. of a fresh 2.5 per cent gelatin solution followed by 3 ml. of 40 per cent formaldehyde solution while shaking well. The reduction is very rapid and the mercury remains in colloidal solution. After 2 minutes, the solution is cooled to room temperature and acetic acid and iodine are added. The mercury dissolves immediately and the excess iodine is back-titrated with thiosulfate. Brindle[479] added, after acidification, 5 ml. of a mixture of 2 parts of ether and 1 part of chloroform. Metallic mercury dissolves within 1 minute and its complete dissolution can be easily observed.

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[475] C. W. Hempel, *Ann.*, **110**, 176 (1859).

[476] E. Rupp, *Arch. Pharm.*, **243**, 300 (1905); *Ber.*, **39**, 3702 (1906); **40**, 3276 (1907).

[477] P. Fleury and J. Marque, *J. pharm. chim.*, (S) **10**, 241 (1929).

[478] M. Fitzgibbon, *Analyst*, **62**, 654 (1937).

(2) Several other methods for the iodometric determination of mercury have been suggested. Ebler[480] reduced mercuric salts in ammoniacal solution with hydrazine sulfate in excess and titrated back by the Stollé method (p. 308). The procedure appears to be very practicable.[481] Feit[482] reduced to metallic mercury in alkaline solution with arsenious oxide and titrated the excess iodometrically.

According to Sloviter *et al.*,[483] Rupp's method[476] gives high results, for iodine reacts slowly with formic acid. They prefer to reduce with hydrazine sulfate in alkaline solution, collect the mercury, and determine bromometrically (p. 523).

Applications of the Mercury Titration: Methods have been developed for the determination of various substances in which they are reacted with a mercuric salt, and the mercurous ion or metallic mercury which is formed is determined iodometrically. For example, monosilane reacts with a solution of mercuric chloride:[484]

$$SiH_4 + 8HgCl_2 + 4H_2O \longrightarrow Si(OH)_4 + 4Hg_2Cl_2 + 8HCl$$

The mercurous chloride is titrated iodometrically. Other organosilicon compounds containing Si—H bonds have been determined. Aldehydes may be determined by oxidizing with potassium mercuric iodide:[485]

$$RCHO + K_2HgI_4 + 2KOH \longrightarrow RCOOH + Hg + 4KI + H_2O$$

The metallic mercury is dissolved in excess of standard iodine solution and back-titrated with thiosulfate. The determination is not affected by most acids, ketones, esters, acetates, ethers, alcohols, epoxides, and organic chlorides.

22. Thallium. According to Proszt,[486] if bromine water is added to a slightly acid solution of a thallous salt until the solution is definitely yellow, all the thallium(I) is converted to the thallic form. The excess bromine is removed with phenol, potassium iodide is added, and the solution is titrated with thiosulfate, starch being used as indicator. The gold color of the separated thallous iodide does not influence the clarity of the end-point change from blue through green to gold. Hatos[487] adapted this procedure for the analysis of rodenticides.

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[479] H. Brindle, *Quarterly J. Pharm. Pharmacol.*, **5**, 432 (1932); *Chem. Abstr.*, **27**, 478 (1933).

[480] E. Ebler, *Z. anorg. Chem.*, **47**, 377 (1906).

[481] For the iodometric determination of small amounts of mercury in organic and inorganic compounds (after reduction with hypophosphorous acid), see R. Robinson, *Analyst*, **54**, 145 (1929).

[482] W. Feit, *Z. anal. Chem.*, **28**, 314 (1889).

[483] H. A. Sloviter, W. M. McNabb, and E. C. Wagner, *Ind. Eng. Chem., Anal. Ed.*, **13**, 890 (1941).

[484] G. Fritz, *Z. anorg. Chem.*, **280**, 134 (1955).

[485] J. E. Ruch and J. B. Johnson, *Anal. Chem.*, **28**, 69 (1956).

[486] J. Proszt, *Z. anal. Chem.*, **73**, 401 (1928); cf. F. Cuta, *Collection Czech Chem. Communs.*, **5**, 287 (1933); **7**, 33 (1935); J. F. Reith and K. W. Gerritsma, *Rec. trav. chim.*, **65**, 770 (1946).

Sill and Peterson[488] determine traces of thallium in solid samples (ores) by dissolving the sample and extracting the thallium in chloroform as the dithizonate.

Deshmukh[489] oxidized thallium(I) with excess of iodine in strongly alkaline solution. After 15 minutes, the dark-brown precipitate of thallic oxide was filtered on a Gooch crucible, the filtrate was acidified with hydrochloric acid, and the excess of iodine titrated with thiosulfate. One milliliter of 0.1*N* thiosulfate corresponds to 10.22 mg. of thallium.

Thallium in Presence of Lead: Mahr and Ohle[490] found that the thallous perchlorate-thiourea complex ($TlClO_4 \cdot 4ThiH$) is very slightly soluble, whereas the lead complex is easily soluble. It is possible to separate thallium from Hg, Ag, Cu, Cd, Fe, Mn, Ni, Co, Cr, Al, Zn, Ba, Sr, and Ca by one precipitation, and from lead by reprecipitation.

Procedure: Add to the thallium solution containing 2 per cent perchloric acid an equal volume of 10 per cent thiourea solution. Shake for 30 minutes at 15°C., filter on a sintered-glass crucible, and wash with a 5 per cent thiourea solution containing a little perchloric acid. Dissolve the precipitate in hot water, acidify with hydrochloric acid, add 0.5 ml. or more of bromine, and boil the solution till the color of bromine disappears. Cool and add 4 drops of bromine water (the solution turns yellow if the oxidation was complete). Remove the excess bromine with 5 ml. of 5 per cent phenol solution, add potassium iodide, and titrate with thiosulfate. The titration of 15–60 mg. of thallium was accurate to about 0.2 per cent.

23. Manganese. ***By Precipitation as Dioxide*** (cf. p. 284): Various methods have been described in the literature for the oxidation of manganese to the dioxide, MnO_2, in acid, neutral, or alkaline medium; the dioxide is filtered, washed, and titrated. The iodometric method is the simplest of those available; the precipitate is dissolved in an acid solution of potassium iodide and titrated with thiosulfate. Should iron be coprecipitated, phosphoric acid or ammonium bifluoride is also added to prevent the reaction of ferric iron with iodide.

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[487] G. Hatos, *Agrártudomány*, 1, 50 (1949)

[488] C. W. Sill and H. E. Peterson, *Anal. Chem.*, 21, 1268 (1949).

[489] G. S. Deshmukh, *Z. anal. Chem.*, 145, 249 (1955).

[490] C. Mahr and H. Ohle, *Z. anal. Chem.*, 115, 254 (1939).

Of course, the dioxide can be titrated in other ways, e.g., by dissolution in excess ferrous sulfate and back-titration with permanganate or dichromate; or by dissolution in arsenious acid and back-titration with permanganate (p. 72).

Kolthoff and Sandell[491] established that oxidation in acid solution is most suitable. However, it should be noted that the ratio of Mn to O in the precipitate is never the theoretical value (1:2) and an empirical factor must be used. It will be seen that the precipitate does have almost the theoretical ratio after oxidation with potassium bromate in presence of iron. In 1901, the oxidation of manganese in acid solution with ammonium or potassium persulfate was suggested.[492] Different workers have tested this method.[493] Kolthoff and Sandell found that even in the presence of much iron difficulties arose, and they preferred to oxidize with bromate. This method yields values which are reproducible to 0.5 per cent.

$$5Mn^{2+} + 2BrO_3^- + 4H_2O \longrightarrow 5MnO_2 + Br_2 + 8H^+$$

Procedure: Add sulfuric or nitric acid to the solution, which should contain 20–150 mg. of manganese, to give an acidity of 0.8–1*N*. If no iron is present in the solution, add 3–5 g. of zinc sulfate. If only a trace of iron is present, add so much pure iron sulfate or nitrate that the amount of iron is at least equal to that of manganese. In this way, the correct composition of the precipitate is ensured and zinc salt need not be added. Add 1–2 g. of potassium bromate and heat to boiling. In iron-free solution, the precipitation is complete after boiling for 5 minutes; if Fe:Mn is less than 10:1, 10 minutes is required, and, if the ratio is greater, 15–20 minutes; if the ratio is 100:1, 30 minutes is necessary and the method becomes troublesome. Replenish the evaporated water as required. After complete precipitation, filter the solution (frequently the first portion of filtrate is slightly turbid but this does not occur on further filtration). Wash the precipitate with six to eight 10 ml. portions of hot water without removing the precipitate quantitatively from the precipitation vessel. Return the filter with the precipitate to the vessel. For iodometric titration add 50–75 ml. of water, 5 ml. of 20 per cent potassium fluoride solution (to complex any iron), 5 ml. of 4*N* sulfuric acid, and 1–2 g. of potassium iodide. Titrate with 0.1*N* thiosulfate, shaking strongly near the end-point so that all the dioxide adhering to the filter is removed.

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[491] I. M. Kolthoff and E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, 1, 181 (1929).

[492] G. von Knorre, *Z. angew Chem.*, **14**, 1149 (1901); **16**, 905 (1903).

[493] M. Geloso, *Ann. Chim.*, **6**, 352 (1926); **7**, 113 (1927); H. Ludert, *Z. angew. Chem.*, **17**, 422 (1904); P. Nicolardot, A. Reglade, and M. Geloso, *Compt. rend.*, **170**, 808 (1920).

Factors: (*a*) Zinc sulfate added, iron absent: 1 ml. of $0.1N$ thiosulfate corresponds to 2.801 mg. of Mn.

(*b*) Iron present: 1 ml. of $0.1N$ thiosulfate corresponds to 2.774 mg. of Mn.

Notes: (1) If the method is used on pure manganese solutions without the addition of zinc or iron, the results are 3.4 per cent lower than the theoretical. In the presence of zinc, the precipitate is nearer the theoretical composition and the deviation decreases to 2 per cent; when iron is present, the deviation is only 1 per cent.

(2) Very small amounts of manganese (2–3 mg.) can be determined by this method with an accuracy of 1 per cent when $0.01N$ thiosulfate is used. Iron in more than one hundred-fold amounts in the presence of traces of manganese can be suitably removed with a suspension of zinc oxide. Precipitation as hydrated iron oxide removes small traces of manganese. The method has been applied to the analysis of steels and ores.[491]

(3) Chromium and vanadium are oxidized to chromate and vanadate but do not interfere because they are found in the filtrate. Vanadate is slightly adsorbed on hydrated manganese dioxide; if large amounts are present, it is better to reduce the precipitate with ferrous sulfate than to use the iodometric method. Phosphoric acid in amounts greater than 1 ml. of $2M$ solution decreases the manganese recovery. Up to 50 mg. of molybdenum or tungsten can be tolerated, but larger amounts of molybdate or tungstate interfere. Nickel, lead, and bismuth do not affect the method. Small amounts of chloride do not interfere because chloride is oxidized by bromic acid. Large quantities of ammonium salts are detrimental, for they decompose bromic acid.

By Conversion to Permanganate: It is well known that manganese salts are oxidized to permanganate by persulfate in nitric acid medium in the presence of silver salt as catalyst. This reaction, which is often used for the colorimetric determination of traces of manganese, gives difficulty in titrimetric use especially with large amounts of manganese because more or less manganese dioxide is formed and precipitates from the solution. Van der Meulen[494] has established that the formation of the dioxide can be prevented if hydrofluoric or phosphoric acid is added; the acids form a soluble complex with the higher oxidation states of manganese. The following method gave very exact results.

Procedure: To a 300 ml. flask add 20 ml. of 20 per cent phosphoric acid, 10 ml. of $0.1N$ silver nitrate, 1 ml. of nitric acid (65%; sp. gr. 1.40–1.42), 2.5 ml. of 35–40 per cent hydrofluoric acid, 2.5 g. of potassium persulfate, and 30 ml. of water. Warm the mixture to 55–60°C. on a water bath. Pipette in a measured amount of the manganese solution corresponding to less than 50 ml. of $0.1N$ permanganate. The solution becomes slightly red on account of the manganese salts but the color disappears on the addition of more manganese, and finally becomes slightly brown. Heat the solution on the bath or over a small flame. After a short time, the color changes from brownish through brownish red to violet-red (permanganate color). An abundant gas evolution indicates the decomposition of persulfate. Boil carefully for 5 minutes, cool, add 50–100 ml. of water and 10 ml. of N potassium iodide, and titrate the liberated iodine with thiosulfate.

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[494] J. H. van der Meulen, *Chem. Weekblad*, 28, 377 (1931).

Note: Iron salts do not interfere, for iron is complexed as phosphate or fluoride. Halides, such as chloride and bromide, must be absent. The permanganate can, of course, also be determined with ferrous sulfate.

24. Miscellaneous Determinations. Sodium borohydride can be assayed rapidly by oxidation with potassium iodate followed by iodometric titration of the excess.[495]

$$3BH_4^- + 4IO_3^- \longrightarrow 4I^- + 3H_2BO_3^- + 3H_2O$$

Procedure: Dissolve a 20–25 mg. sample of sodium borohydride in 25 ml of 0.5N sodium hydroxide. Add 35 ml. of 0.25N potassium iodate immediately, and swirl vigorously for 30 seconds. Add 2 g. of potassium iodide, followed by 20 ml. of 4N sulfuric acid. Allow to stand in darkness for 2–3 minutes and titrate the liberated iodine with 0.10N sodium thiosulfate (starch indicator).

Notes: (1) Sodium borohydride is hygroscopic; therefore suitable precautions must be taken in handling it. A dry box may be used, or a larger sample may be weighed quickly and dissolved in a proportionately larger amount of 0.5N sodium hydroxide, from which an aliquot containing approximately 20–25 mg. of sodium borohydride is taken.

(2) The weight of sodium borohydride can be calculated by means of the following formula:

$$\text{Mg. of } NaBH_4 = (\text{ml. of } KIO_3 \times \text{normality} - \text{ml. of } Na_2S_2O_3 \times \text{normality}) \times 4.731$$

Lithium aluminium hydride can be determined by the addition of excess iodine and back-titration with thiosulfate.[496] Direct titration gives very low results.

Procedure: Add the hydride solution (containing about 1 millimole of $LiAlH_4$) rapidly, while shaking, to 20 ml. of 0.4N iodine in benzene. Dilute with water, add some drops of acetic acid, and titrate the excess of iodine with 0.1N thiosulfate.

Notes: (1) Solutions 0.1–1M in lithium aluminum hydride can be determined in this way.

(2) It is also possible to measure the hydrogen evolved in an apparatus similar to that used for the determination of active hydrogen.

A somewhat similar procedure has been described for the determination of organomagnesium compounds.[497] The original papers should be consulted for details.

[495] D. A. Lyttle, E. H. Jensen, and W. A. Struck, *Anal. Chem.*, **24**, 1843 (1952).

[496] H. Felkin, *Bull. soc. chim. France*, 1951, 347.

[497] G. Champetier and R. Kullman, *Bull. soc. chim. France*, **16**, 693 (1949); cf. P. Jolibois, *Compt. rend.*, **155**, 213 (1912); A. Job and R. Reich, *Bull. soc. chim. France*, (4) **33**, 1414 (1923); H. Gilman, P. D. Wilkinson, W. P. Fishel, and C. H. Meyers, *J. Am. Chem. Soc.*, **45**, 150 (1923).

CHAPTER VIII

IODOMETRIC DETERMINATION OF ORGANIC COMPOUNDS

1. Aldehyde Groups. Under suitable conditions aldehyde compounds are quantitatively oxidized by hypoiodite to the corresponding carboxylic acids. The determination of formaldehyde, chloraldehyde, and aldoses can be based on this reaction.

Formaldehyde: An elegant and generally applicable method for pure formaldehyde solutions was developed by Romijn.[1]

Procedure: To 10 ml. of aqueous formalin solution (2–3 g. of formalin diluted to 500 ml.), add 25 ml. of 0.1N iodine and at least 2 ml. of 4N sodium hydroxide. After 5 minutes, acidify with hydrochloric acid and titrate the liberated iodine with 0.1N thiosulfate. One milliliter of 0.1N iodine corresponds to 1.5 mg. of HCOH.

Notes: (1) The method is very accurate. The excess of iodine and hydroxide need only be small. Even with 0.01N and more dilute solution, the results are very satisfactory.[2] According to Signer,[3] formaldehyde in very dilute solutions is but slowly oxidized quantitatively. He recommended the use of 20 ml. of solution containing about 0.1 per cent of formaldehyde with 20 ml. of 0.2N iodine (a very large excess) and 5 ml. of 2N sodium hydroxide. After 1–2 hours, 2 ml. of concentrated hydrochloric acid and about 100 ml. of water were added and the solution was back-titrated with 0.1N thiosulfate. Of course, the use of such a large excess of iodine is objectionable from the point of view of accuracy.

(2) Ethanol, acetone, and acetaldehyde interfere in the determination because they consume iodine, but methanol, formic acid, and acetic acid have no influence on the result.[2] Mach and Herrmann[4] have thoroughly examined the iodometric determination of formaldehyde in presence of acetone and acetaldehyde; the original paper should be consulted for details.

Chloral Hydrate: Rupp[5] proposed an iodometric determination of chloral hydrate, but the method was found to be unsatisfactory.[6] The following method gives exact results.

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[1] G. Romijn, *Z. anal. Chem.*, 36, 18 (1897); 39, 60 (1900).

[2] For a review of the early literature, see F. Mach and R. Herrmann, *Z. anal. Chem.*, 62, 104 (1923).

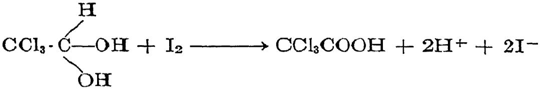
[3] R. Signer, *Helv. Chim. Acta*, 13, 43 (1930).

[4] F. Mach and R. Herrmann, *Z. anal. Chem.*, 63, 417 (1923)

[5] E. Rupp, *Arch. Pharm.*, 241, 328 (1903).

[6] I. M. Kolthoff, *Pharm. Weekblad*, 60, 2 (1923).

Procedure: To 25 ml. of $0.1N$ iodine, add 10 ml. of $2N$ sodium carbonate and then 10 ml. of $0.1M$ chloral hydrate solution (chloral hydrate decomposes to chloroform if the order of addition is altered). Stopper the flask and allow to stand for 1 hour. Acidify with hydrochloric acid and back-titrate the excess of iodine with $0.1N$ thiosulfate. One milliliter of $0.1N$ iodine corresponds to 8.27 mg. of $CCl_3COH \cdot H_2O$:



$$CCl_3 \cdot C(H)(OH)—OH + I_2 \longrightarrow CCl_3COOH + 2H^+ + 2I^-$$

Note: Schwicker[7] used 10 ml. of N ammonium borate solution (170 ml. of 10 per cent ammonia and 20 g. of boric acid per liter) instead of sodium carbonate. The solution was acidified after standing for 15 minutes. The oxidation can also be carried out with hypobromite, excess of which is back-titrated with arsenious acid.

2. Aldoses. Since the iodometric determination of aldoses can be applied to the analysis of different varieties of sugar, it will be considered in some detail. Romijn[8] was the first to note that aldoses were oxidized by hypoiodite to the corresponding carboxylic acid; iodine itself has no oxidizing effect. The reaction takes place in weakly alkaline solution where the hypoiodite is most stable and the aldose is less exposed to decomposition by hydroxyl ions than in strong alkaline medium. Romijn also found that fructose (a ketone) was scarcely attacked, although saccharose, raffinose, and stachyose are very troublesome in the determination of aldoses. Other organic materials such as methanol, formic acid, glycerin (glycerol), mannitol, lactic acid also interfere considerably. This iodometric determination is therefore much less preferable than the determination of sugars using alkaline copper solution. Bougault[9] improved the method of Romijn; we shall consider this later.

No further investigations were pursued for some time until, in 1914, Bland and Lloyd[10] proposed the following method. To a mixture of 50 ml. of $0.1N$ sodium hydroxide and 50 ml. of $0.1N$ iodine was added the sugar test solution. After a standing time of 5 minutes to 24 hours, the solution was acidified and back-titrated with thiosulfate. On principle it is not advisable to prepare beforehand a mixture of iodine and caustic soda because a large part of the iodine is converted to iodate. The method was improved by Willstätter and Schudel,[11] who added to the mixture of glucose and iodine so much hydroxide that the gluconic acid produced was tied up but the sugar chain itself was not attacked. The reaction which occurs is given in the following equation:

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[7] A. Schwicker, *Z. anal. Chem.*, **110**, 161 (1937).

[8] G. Romijn, *Z. anal. Chem.*, **36**, 349 (1897).

[9] J. Bougault, *J. pharm. chim.*, **16**, 97, 313 (1917).

[10] N. Bland and L. L. Lloyd, *J. Soc. Chem. Ind.*, **32**, 948 (1914).

$$\mathrm{RCOH} + \mathrm{I_2} + 3\mathrm{NaOH} \longrightarrow \mathrm{RCOONa} + 2\mathrm{NaI} + 2\mathrm{H_2O}$$

Willstätter and Schudel add 1.5–4 times the theoretical amount of iodine to the sugar solution and then add 1.5 times the theoretical amount of sodium hydroxide with shaking. After 12–15 minutes, the mixture is acidified with sulfuric acid and titrated with thiosulfate. One hundred milligrams of glucose consumed 11.11 ml. of $0.1N$ thiosulfate.

Judd[12] further investigated the iodometric determination of aldoses and found that under no conditions was the oxidation to carboxylic acid quantitative. Baker and Fulton[13] agreed with this finding but held that the method was very useful with an empirical factor. Kolthoff[14] studied the aldose titration and recommended the following method.

Procedure (*a*): Mix 10 ml. of the sugar solution containing a maximum of 1.1 per cent of glucose with 25 ml. of $0.1N$ iodine solution and add with shaking 30 ml. of $0.1N$ sodium hydroxide. Stopper the flask and set aside for 3–10 minutes. Acidify with dilute sulfuric or hydrochloric acid and back-titrate with thiosulfate. Even with 10 times more dilute glucose solution, the method gives satisfactory results: in this case, 25 ml. of $0.01N$ iodine and 5 ml. of $0.1N$ hydroxide are used and the iodine is back-titrated after 10 minutes.

Notes: (1) Galactose, arabinose, and maltose[15] can be determined in exactly the same way as glucose. The reaction between lactose and hypoiodite is slower; 10 minutes are allowed before back-titration; a small excess of hydroxide is much more harmful here than in the determination of glucose.

(2) Various organic compounds other than aldoses also consume some iodine (see also Romijn). In the above method, 1 g. of the following compounds consumes the number of milliliters of $0.1N$ iodine solution which is given in parentheses: fructose (1.2), mannitol (0.8), glycerin (1.4), sodium lactate (1.0), sodium formate (0.15), urea (0.08), dextrin (12). The interference of saccharose decreases relatively with increasing concentration. In 5 per cent solution, 1 g. of saccharose

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[11] R. Willstätter and G. Schudel, *Ber.*, 51, 780 (1918); for the time of standing see H. S. Miller, *Ind. Eng. Chem., Anal. Ed.*, 9, 37 (1937).

[12] H. M. Judd, *Biochem. J.*, 14, 255 (1920).

[13] J. L. Baker and H. F. E. Fulton, *Biochem. J.*, 14, 754 (1920).

[14] I. M. Kolthoff, *Z. Untersuch. Nahr. Genuss.*, 45, 131 (1923).

[15] For the maltose determination, see W. Braun and B. Bleyer, *Z. anal. Chem.*, 76, 1 (1929).

consumed about 0.6 ml. of $0.1N$ iodine solution; in 10 per cent solution, 0.5 ml., and at higher concentrations, 0.35 ml. per gram.

If the amount of saccharose is less than 11 times the amount of glucose, no real error results. For an unsuitable ratio of the materials, it is best to determine the necessary correction with a mixture of known composition; this increases greatly with temperature.[14]

Fructose has a much more harmful effect than saccharose; this may well be connected with the well-known rearrangement of fructose to glucose and mannose in slightly alkaline solution. (Pauchard[16] used the method of Bougault at 0°C., when fructose does not interfere; the back-titration was carried out after 2.5 hours.) For invert sugar, 1 per cent of the obtained value is subtracted to account for the fructose.

The Carbonate Method of Bougault: Independently of Romijn, Bougault[17] developed the following method. To 25 ml. of the 1 per cent aldose solution are added 50 ml. of $0.16N$ iodine solution and 50 ml. of 15 per cent sodium carbonate solution. After 30 minutes, the aldose is quantitatively converted to the carboxylic acid but a little more iodine is also consumed which, according to Bougault, is substituted in the organic molecule. The last reaction occurs with all non-aldehyde sugars and a correction must therefore always be made. Of course, Bougault used a very large excess of iodine; if this is avoided, Kolthoff found that the amount of organically bound iodine is quite negligible for aldoses. A mixture of sodium carbonate and bicarbonate can be substituted for carbonate but quantitative oxidation is then slower. Colin and Liéven[18] preferred a mixture of secondary and tertiary sodium phosphate and back-titrated after 1 hour, but there appears to be no advantage. A buffer mixture of sodium carbonate and borax has also been proposed.[19] Kolthoff found that a modified method gave good results for glucose, galactose, maltose, lactose, rhamnose, and arabinose.

Procedure (*b*): To 10 ml. of approximately $0.05M$ aldose solution, add 25 ml. of $0.1N$ iodine and 15 ml of $1N$ sodium carbonate. Stopper the flask and set aside for 20–30 minutes. Acidify with hydrochloric or sulfuric acid and titrate the excess of iodine with $0.1N$ thiosulfate.

Notes: (1) The interference of foreign materials is different from that of the "iodine-sodium hydroxide" method. The influence of saccharose is much smaller; 2 g. of saccharose in the presence of 90 mg. of glucose does not cause a noticeable error, but 3 g. causes a positive error of 1 per cent. The carbonate method is thus to be preferred when saccharose is present. This is also true of the determination of lactose in presence of cane sugar. Fructose causes approximately the same error in both methods; if the amount of fructose is known, an appropriate correction can be made. Dextrin and mannitol have similar reduction values in both methods. The interference of glycerol is only half as large in the carbonate method, whereas formate surprisingly consumes exactly 7 times as much iodine as it does in the hydroxide method. Lactate has the same effect in both methods.

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[16] E. Pauchard, *J. pharm. chim.*, (8) **3**, 248 (1926).

[17] J. Bougault, *J. pharm. chim.*, **16**, 97, 313 (1917).

[18] H. Colin and O. Liéven, *Bull. soc. chim. France*, (4) **23**, 430 (1918).

[19] D. T. Englis and W. J. Byer, *Ind. Eng. Chem., Anal. Ed.*, **2**, 121 (1930)

According to Dykins and Englis,[20] an alkaline glycocoll (glycine) solution is partly oxidized by iodine. The reaction rate of hypoiodite with glucose is so great that amino acids do not interfere, although these can form compounds with monoses. When the glycocoll content of the solution is known, the correction can be determined empirically by a blank determination.

(2) The analytical methods described for the aldoses have been used for the analysis of different foodstuffs, e.g., for the determination of lactose in milk serums and of glucose in honey.[21]

Collins[22] has discussed the difficulties which arise from the slow oxidation of mannose. Secondary reactions become appreciable as the oxidation is taken to completion; generally they consist of interconversion of aldoses and ketones and the formation of iodate. By suitable control of the experimental conditions the extent of secondary reactions can be maintained at a low and constant figure.

Procedure: To $^1/_{80}$ mole of sugar, add equal volumes of N sodium carbonate solution and $0.1N$ iodine solution (containing 60 g. of potassium iodide per liter). Maintain the solution at 20°C. for 30 minutes after the first addition of iodine and then acidify with $6N$ hydrochloric acid. Titrate the excess of iodine with $0.1N$ thiosulfate; the titer should be between 28 and 32 ml.

The iodine used, t, is the difference between this value and that of a blank determination without sugar. The percentage of aldose, p, is given by

$$t = 0.45 + 0.2445p$$

where the predominant aldose is mannose, and by

$$t = 0.45 + 0.2490p$$

when the predominant aldose is glucose.

When a mixture of aldoses is present and the composition is known approximately, the above formulae can be interpolated.

Determination of Fructose in Presence of Glucose:[23] To a suitable portion of the solution, add enough $0.2N$ iodine and sodium hydroxide (see p. 377)

[20] F. A. Dykins and D. T. Englis, *Ind. Eng. Chem., Anal. Ed.*, **3**, 21 (1931).

[21] See A. Behre, *Z. Untersuch. Nahr. Genussm*, **41**, 226 (1921); G. Borries, *Z. Untersuch. Lebensm.*, **5**, 405 (1928); F. Auerbach and E. Bodländer, *Z. angew. Chem.*, **36**, 602 (1923); F. Auerbach and G. Borries, *Arbb. Reichsgesundh.*, **57**, 318 (1926); K. D. Dekker, *Arch. Suikerind. Ned. Indië*, 1928, 699. For the determination of xylose, see C. S. Slater and S. F. Acree, *Ind. Eng. Chem., Anal. Ed.*, **2**, 274 (1930); these authors determine not only the reduced iodine but also the amount of sodium hydroxide consumed.

[22] J. R. Collins, *Anal. Chim. Acta*, **9**, 500 (1953).

[23] I. M. Kolthoff, *Z. Untersuch. Nahr. Genussm.*, **45**, 141 (1923).

for the oxidation of the glucose. After 5 minutes, acidify slightly with hydrochloric acid and remove the bulk of the excess of iodine at first with a 10 per cent solution of sodium sulfite and, when the solution has become only slightly yellow, remove the remainder with a 1 per cent solution. Neutralize the solution to methyl orange, dilute to 100 ml., and determine the fructose in an aliquot by the method of Schoorl (p.) 361.

Notes: (1) The excess of iodine cannot be reduced by thiosulfate because the tetrathionate produced reacts further in the fructose determination and leads to many difficulties.

(2) Kruisheer[24] investigated the method thoroughly and used it for the determination of fructose in "starch syrup." In many cases, for example in the analysis of foodstuffs, it is recommended that the volume for the oxidation of glucose be not too large. Kruisheer[24] and Mees[25] therefore used 1*N* iodine solution and 1*N* or 4*N* sodium hydroxide for the oxidation.

For the determination of saccharose in starch syrup, the method gives good results.[26] Fructose in urine has also been determined.[27]

The original papers should be consulted for details.

3. Acetone. In alkaline solution, acetone is converted to iodoform by hypoiodite:

$$CH_3COCH_3 + KIO \longrightarrow CHI_3 + CH_3COOK + 2KOH$$

One millimole of acetone consumes 6 milliequivalents of iodine; thus, 1 ml. of 0.1*N* iodine corresponds to 0.967 mg. of acetone.

On this basis, Messinger[28] proposed his well-known iodometric determination. The method has been much tested, especially by Geelmuyden,[29] and is in Kolthoff's experience wholly to be recommended.

Procedure: To 10 ml. of less than 0.03*M* acetone solution, add 5 ml. of 4*N*, or at least 25 ml. of 1*N* sodium hydroxide and 25 ml. of 0.1*N* iodine.

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[24] C. I. Kruisheer, *Chem. Weekblad,* **23**, 431 (1926); **26**, 254 (1929).

[25] R. T. A. Mees, *Chem. Weekblad,* **25**, 674 (1928).

[26] J. D. Filippo, *Chem. Weekblad,* **25**, 676 (1928).

[27] C. I. Kruisheer, *Biochem. Z.,* **207**, 441 (1929).

[28] J. Messinger, *Ber.,* **21**, 3366 (1888).

[29] H. C. Geelmuyden, *Z. anal. Chem.,* **35**, 503 (1896); cf. A. P. Sy, *J. Am. Chem. Soc.,* **29**, 786 (1907); A. J. Field, *Ind. Eng. Chem.,* **10**, 552 (1918). L. F. Goodwin, *J. Am. Chem. Soc.,* **42**, 39 (1920), states that the method gives excellent results if the procedure given by F. Collischonn, *Z. anal. Chem.,* **29**, 562 (1890), is followed exactly. For the determination of acetone in mixtures with ethanol, see J. H. Bushill, *J. Soc. Chem. Ind.,* **42**, 216 (1923); J. N. Rakshit, *Analyst,* **41**, 245 (1916); J. H. Northrop, L. H. Ashe, and J. K. Senior, *J. Biol. Chem.,* **39**, 1 (1919). For the application of the method to the determination of carbonyl groups in ketoses and a systematic examination of the acetone determination, see F. Collischonn, *Z. anal. Chem.,* **29**, 562 (1890); H. Elsner, *Ber.,* **61**, 2364 (1928)

Shake thoroughly and set aside for 10 minutes. Acidify with hydrochloric acid and titrate the excess of iodine with 0.1*N* thiosulfate.

Notes: (1) An excess of hydrochloric acid causes no difficulty—in contrast to different opinions expressed in the literature.

(2) Haughton[30] found that the Messinger method gave results 2–2.5 per cent high. This was ascribed to side reactions, by which a small part of the acetone was converted to formate.

$$CH_3COCH_3 + 5NaOH + 10I \longrightarrow 2CHI_3 + HCOONa + 4NaI + 4H_2O$$

Haughton was able to detect a little formate in the reaction products.

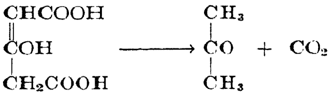
(3) The method described is also very suitable for more dilute solutions. Since methanol is completely indifferent to the reaction, the method can be applied to the determination of acetone in wood alcohol. Acetaldehyde and ethanol[31] and also aldoses interfere. If acetone is to be determined in the presence of nonvolatile compounds which consume hypoiodite, it can be distilled previously with ice-cooling.

In presence of acetaldehyde, Kogan[32] added sulfuric acid and permanganate to the solution. The aldehyde is oxidized while the acetone remains unattacked. The solution is bleached with hydrogen peroxide, made alkaline and the excess of peroxide is removed with manganous salt. The acetone is then determined iodometrically in the filtrate.

Applications of the Acetone Determination: Different organic compounds can be converted to acetone by suitable oxidation methods. Thus Kemal[33] converted isopropyl alcohol to acetone; he added 0.4 g. of powdered potassium dichromate and 3 ml. of *N* sulfuric acid to 15 ml. of 0.1*N* solution (1 g. of alcohol per liter) and shook until the dichromate dissolved. After 24 hours, the solution was made alkaline with sodium hydroxide, and the acetone was distilled off and determined in the distillate.

Chlorobutanol in oil solutions can be assayed by hydrolyzing and distilling off the acetone so formed.[34] This may then be determined by the iodometric method.

Kogan[32] applied the acetone determination to citric acid. In the presence of acetic acid, citric acid is oxidized to acetone dicarboxylic acid in boiling solution; this decomposes to acetone and carbon dioxide.



$$\begin{array}{l} CHCOOH \\ \Vert \\ COH \\ | \\ CH_2COOH \end{array} \longrightarrow \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array} + CO_2$$

The acetone is determined iodometrically. The method is purely empirical and the calculations must be based on determinations with pure citric acid.

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[30] C. O. Haughton, *Ind. Eng. Chem., Anal. Ed.*, 9, 167 (1937).

[31] Cf. G. Heikel, *Chem.-Ztg.*, **32**, 75 (1908); E. R. Squibb, *J. Am. Chem. Soc.*, **18**, 1068 (1896).

[32] A. I. Kogan, *Z. anal. Chem.*, **80**, 112 (1930).

[33] H. Kemal, *Z. anal. Chem.*, **107**, 33 (1936); cf. H. A. Cassar, *Ind. Eng. Chem., Anal. Ed.*, 19, 1061 (1927); C. J. Frisone, *Anal. Chem.*, **26**, 924 (1954).

[34] H. Jensen and P. Jannke, *J. Am. Pharm. Assoc.*, **37**, 38 (1948).

Täufel and Mayr[35] thoroughly investigated this method for citric acid. Various factors have a great influence on the quantitative production of acetone. A pH range of 1.9–2.3 is the optimum for the oxidation and distillation; thus the loss of acetone by oxidation of the intermediately formed acetone dicarboxylic acid is kept to a minimum while the decarboxylation proceeds very swiftly.

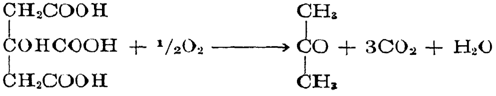
Apparatus: Fit a glass-stoppered flask with a distillation attachment which consists of a dropping funnel with a glass stopcock and a bulb to prevent spray from being carried over. The outlet of the dropping funnel is sealed into the wide part of the distillation tube so that liquid can be introduced into the flask during the distillation. Then the outlet from the bulb bends to the vertical and discharges in a spiral condenser.

An adapter is fitted by a ground-glass joint so that it dips into the absorption solution in the receiver.

Procedure: Place the citric acid test solution in the distillation flask and add water to give a final volume of 50–100 ml. For each 50 ml. of liquid add 2–3 ml. of buffer solution (49.03 g. of 100 per cent phosphoric acid and 68.08 g. of potassium dihydrogen phosphate) and a few boiling stones. Attach the flask under light pressure with springs to the distillation tube. Place 0.05 per cent potassium permanganate solution in the dropping funnel and an exactly measured amount of approximately $2N$ potassium hydroxide (about 15 ml.) in the absorption vessel, which is cooled with ice. Heat the liquid in the flask to boiling and, when all the air has been driven out, open the cock of the funnel carefully and allow the permanganate to enter at a rate of about 1 drop per second. The dropping must be carefully regulated so that each drop is bleached before the entry of the next drop. Continue the oxidation until the permanganate color, or the separation of manganese dioxide, remains for at least 5 minutes. Without further addition of permanganate, boil the solution strongly for 15–20 minutes. Remove the absorption vessel taking care that the liquid does not suck back and rinse the condenser with distilled water. Determine the acetone in the distillate by adding with constant shaking so much $0.1N$ iodine solution that at least one fifth of the amount used remains in excess. Stopper the flask and after 20–30 minutes, during which time the solution is shaken frequently, acidify, and back-titrate with $0.1N$ thiosulfate.

A blank determination must be run on the potassium hydroxide used. One milliliter of $0.1N$ iodine corresponds to 3.201 mg. of citric acid or 3.501 mg. of the monohydrate crystalline acid.

Notes: (1) According to Täufel and Mayr,[35] the *theoretical yield* of acetone is obtained.



$$\begin{array}{l}CH_2COOH\\ |\\ COHCOOH\\ |\\ CH_2COOH\end{array} + {}^1/_2O_2 \longrightarrow \begin{array}{l}CH_3\\ |\\ CO\\ |\\ CH_3\end{array} + 3CO_2 + H_2O$$

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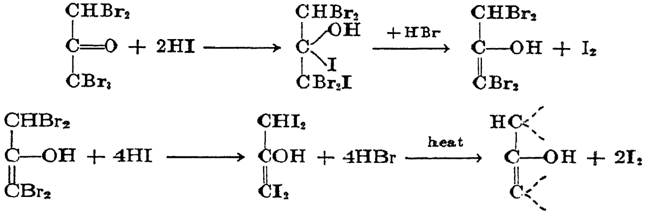
[35] K. Täufel and F. Mayr, *Z. anal. Chem.*, **93**, 1 (1933).

The method can also be used for the determination of citric acid in wine. The original paper should be consulted for details.

(2) Kometiani[36] oxidized citric acid to pentabromoacetone, which reacts with alcoholic hydriodic acid in the following way:



$$CHBr_2-CO-CBr_3 + 2HI \longrightarrow CHBr_2-C(OH)(I)-CBr_2I \xrightarrow{+HBr} CHBr_2-C(OH)=CBr_3 + I_2$$

$$CHBr_2-C(OH)=CBr_2 + 4HI \longrightarrow CHI_2-C(OH)=CI_2 + 4HBr \xrightarrow{heat} HC{<}-C(OH)=C{<} + 2I_2$$

The method is not capable of great accuracy (about 3–5 per cent); for details, Kometiani's interesting paper should be consulted.

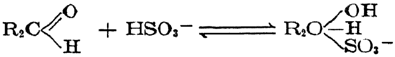
(3) In the presence of various organic materials, such as tartaric acid, lactic acid, and sugars, acetaldehyde is formed by the distillation with permanganate. This must be removed by oxidation with permanganate, before the titration of acetone.

Acetylmethylcarbinol: According to Langlykke and Peterson,[37] acetylmethylcarbinol can also be determined by the Messinger method:

$$CH_3COHCOCH_3 + 3NaOI \longrightarrow CHI_3 + CH_3HOHCOONa + 2NaOH$$

After the addition of iodine to the alkaline solution, the mixture is allowed to stand for 15 minutes, and then is acidified and back-titrated. These authors also described a distillation method for the separation of acetone, alcohol, and reducing sugars.

4. Determination of Carbonyl Groups with Bisulfite. The following reaction takes place between carbonyl groups and bisulfite:



$$R_2C{<}^{O}_{H} + HSO_3^- \rightleftharpoons R_2O{<}^{OH}_{H\;SO_3^-}$$

This reaction has been thoroughly discussed in Vol. I (p. 213).

The iodometric determination of carbonyl groups by this means was suggested by Ripper.[38] He recommended the use of a 0.5 per cent aqueous (as much as possible) solution of the aldehyde; 25 ml. of this solution was run into 50 ml. of potassium bisulfite solution (12 g. of $KHSO_3$ per liter). The flask was closed and after 15 minutes the unconsumed bisulfite was titrated with 0.1N iodine. Ripper obtained satisfactory results with acetaldehyde, formaldehyde, benzaldehyde, and vanillin. Rocques[39] advised that the acetaldehyde determination be carried out in 50 per cent alcoholic solution. Jolles[40] applied the method to the analysis of furfurals and pentoses.

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[36] P. A. Kometiani, *Z. anal. Chem.*, 86, 359 (1931).

[37] A. F. Langlykke and W. H. Peterson, *Ind. Eng. Chem., Anal. Ed.*, 9, 163 (1937).

[38] M. Ripper, *Monatsh.*, 22, 1079 (1900); cf. S. L. Langedijk, *Rec. trav. chim.*, 46, 218 (1927).

A systematic investigation of the method has not been carried out. Kolthoff believes that considerable errors would result from the atmospheric oxidation of the bisulfite; it would be better to stabilize the solution by the addition of 5–10 per cent of alcohol. A further error through atmospheric oxidation also arises during the back-titration with iodine. Kolthoff could only obtain satisfactory results if after the decomposition the aldehyde-bisulfite mixture was poured into a large amount of iodine solution which was then back-titrated with thiosulfate. The titer of the bisulfite solution was obtained in the same way.

Procedure: To a suitable amount of the aldehyde solution, add a 30–50 per cent excess of bisulfite solution (containing 5 per cent of alcohol) and set aside for 15–30 minutes. Pipette 25 ml. of 0.1N iodine into another flask and add the aldehyde-bisulfite mixture. Back-titrate immediately with 0.1N thiosulfate solution.

Notes: (1) For formaldehyde and acetaldehyde, the method is very accurate; and even with 0.01N solutions, if 30 minutes are allowed before the back-titration. With benzaldehyde and 0.1N solutions the error is 1 per cent; with more dilute solutions it is greater. A larger addition of alcohol has very little influence.

(2) For the determination of traces of formaldehyde in air Goldman and Yagoda[41] transform the aldehyde with bisulfite into the addition compound, decompose the excess of bisulfite with iodine at pH 6 to 7, and subsequently liberate the sulfite from the addition compound by the addition of sodium carbonate and sodium acetate. The sulfite is then titrated with iodine.

Quite generally, the rate of decomposition of an aldehyde-bisulfite addition compound is so small at the correct pH (near 3) that the excess of bisulfite can be removed with iodine (preferably at 0°C.) without the reaction product being attacked. The "bound" bisulfite can then be determined iodometrically at the proper pH (see method of Donnally, p. 385).

(3) Parkinson and Wagner[42] investigated the method thoroughly and obtained satisfactory results. For the determination of aromatic aldehydes they recommend that the solution be cooled in ice before the back-titration with iodine, which should also be done in the cold.

(4) Benzaldehyde in bitter almond water cannot be determined in this way because hydrogen cyanide interferes by forming benzaldehyde cyanohydrin. Acetone also cannot be present because the complex dissociation constant of its bisulfite compound is too large (see Vol. I, p. 215).

(5) The method is accurate to about 2 per cent for furfural, if 0.1N solutions are used and at least a three-fold excess of bisulfite is added.

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[39] X. Rocques, *Compt. rend.*, **127**, 524, 764 (1898).

[40] A. Jolles, *Z. anal. Chem.*, **45**, 196 (1906).

[41] F. H. Goldman and H. Yagoda, *Ind. Eng. Chem., Anal. Ed.*, **15**, 377 (1943)

[42] A. E. Parkinson and E. C. Wagner, *Ind. Eng. Chem., Anal. Ed.*, **6**, 433 (1934).

Donnally[43] preferred to determine directly the bisulfite combined with the aldehyde. Thus no standard solution of bisulfite is required and the air-oxidation of bisulfite has no influence on the result.

Procedure: To the formaldehyde or benzaldehyde solution, add 5 ml. of 1*M* sodium bicarbonate and 30 ml. of 0.1*M* sodium bisulfite (about 30 per cent excess). At the pH of this solution, the reaction rate is quite fast and equivalence is attained in 15 minutes. After this time, add 10 ml. of 1*M* acetic acid or, for benzaldehyde, 10 ml. of 1*M* phosphoric acid, and 2 ml. of starch solution. Remove the excess of bisulfite with iodine-potassium iodide solution until the starch just develops a blue color. Add 10 ml. of 1*M* sodium carbonate and titrate slowly with standard iodine solution to a permanent end-point. In the final titration, the bisulfite combined with the aldehyde is titrated.

Note: For the formation of the addition product and the titration of the bisulfite the pH is such that the reaction rate is rapid. The removal of the excess of bisulfite is done in slightly acid solution, when the decomposition rate of the complex is at a minimum. The method is accurate to 0.1 per cent for formaldehyde and to 1 per cent for benzaldehyde. The fundamental theory has been discussed in Vol. I (p. 213).

5. Nitrogen Compounds. ***Semicarbazide:*** Semicarbazide is quantitatively converted by iodine to nitrogen, ammonia, and carbon dioxide;

$$NH_2NHCONH_2 + 2I_2 + H_2O \longrightarrow N_2 + CO_2 + NH_4I + 3HI$$

Bartlett[44] found the reaction to be bimolecular, and at pH values of less than 5 its rate is proportional to the concentration of the undissociated semicarbazide. However, the reaction is faster at pH 7, when a simple iodometric determination is possible.

Procedure: To 20 ml. of 0.5*M* phosphate buffer solution of pH 7 (if the test solution is acid, first neutralize to pH 7 with disodium hydrogen phosphate) add sufficient 0.04–0.05*N* iodine so that after the reaction an excess of about 2.5 ml. is present. Add the measured semicarbazide solution to the mixture and back-titrate with thiosulfate.

Notes: (1) Probably it would be simpler to add the iodine to the semicarbazide-buffer mixture until a definite excess is present and then back-titrate.

(2) Glyoxal and glyoxalic acid in the presence of other organic acids may be determined by adding a known excess of semicarbazide hydrochloride, treating the excess with standard potassium iodate and titrating with thiosulfate.[45]

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[43] L. H. Donnally, *Ind. Eng. Chem., Anal. Ed.*, 5, 91 (1933).

[44] P. D. Bartlett, *J. Am. Chem. Soc.*, **54**, 2853 (1932).

[45] F. Salzer, *Z. anal. Chem.*, **146**, 260 (1955).

Thiosemicarbazide: In alkaline solution, thiosemicarbazide is quantitatively oxidized by iodine in less than 30 minutes.[46]

$$CSNH_2(NHNH_2) + 6I_2 + 5H_2O \longrightarrow 12HI + HCNO + N_2 + H_2SO_4$$

The excess of iodine is back-titrated with thiosulfate. In bicarbonate solution the oxidation requires 8–10 hours; 1 mole of thiosemicarbazide requires only 10 equivalents of iodine because HCN is formed instead of HCNO. Hydrocyanic acid reacts partly with iodine in bicarbonate solution to form iodine cyanide, which is, however, quantitatively titrated as free iodine in acid solution.

6. Sulfur-Containing Compounds. ***Carbon Disulfide:*** Carbon disulfide is quantitatively converted in alcoholic potassium hydroxide solution to xanthogenate. This reacts rapidly and quantitatively with iodine in neutral solution to form dixanthogen:

$$CS_2 + KOH + C_2H_5OH \longrightarrow SC(OC_2H_5)SK + H_2O$$

$$2SC(OC_2H_5)SK + I_2 \longrightarrow 2KI + (SCOC_2H_5S)_2$$

Procedure:[47] Dissolve a weighed amount of the solution in 1–2 ml. of freshly prepared alcoholic hydroxide solution (the sample is placed in a thin-walled glass capsule which is broken under the caustic solution) and add N acetic acid until phenolphthalein is bleached but the solution is still alkaline to litmus. Add starch immediately and titrate with $0.01N$ iodine.

Notes: (1) The method gives accurate results even with very small amounts of carbon disulfide (1 mg.). Compounds which react with iodine interfere and must be removed (alternatively, the iodine consumption could be determined on a blank determination).

(2) Bishop and Wallace[48] tried to determine carbon disulfide in the presence of carbon tetrachloride by this method but the end-point was difficult to detect. Direct titration with $0.001N$ iodine yielded good results when the dead-stop end-point was used.

Bang and Szybalski[49] allowed a certain time of standing to make the reaction quantitative and gave a procedure by which carbon disulfide in water can be determined.

Reagent: Ten per cent potassium hydroxide in 96 per cent ethanol prepared at low temperature. Store in an ice box.[50]

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[46] A. Gaffre, *Ann. fals. et fraudes*, 22, 90 (1929); *J. pharm. chim.*, (8) 9, 19 (1929).

[47] M. P. Matuszak, *Ind. Eng. Chem., Anal. Ed.*, 4, 98 (1932); previous literature is given in this paper.

[48] R. L. Bishop and E. L. Wallace, *Ind. Eng. Chem., Anal. Ed.*, 17, 563 (1945).

[49] N. H. Bang and W. Szybalski, *Acta Chem. Scand.*, 3, 926 (1949).

[50] J. R. Harrower and F. H. Wiley, *J. Ind. Hyg. Toxicol*, 19, 486 (1937).

Procedure: Introduce into a 300 ml. glass-stoppered Erlenmeyer flask 20 ml. of alcoholic alkali solution and pipette in 10 ml. of aqueous carbon disulfide solution. Close the flask, shake, and allow to stand in the dark for 30 minutes. Remove the stopper, wash with a little water, add a drop of phenolphthalein, and 60 per cent acetic acid dropwise until the indicator is colorless, and then 3 drops in excess. Add 1 g. of calcium carbonate, shake for about 15 seconds, add 1 ml. of starch solution, dilute with water to 150 ml. and titrate with 0.01*N* iodine until the color is dark blue (about 0.5 ml. excess). Back-titrate with 0.01*N* thiosulfate. Run a blank, substituting 10 ml. of water for 10 ml. of aqueous carbon disulfide solution.

Xanthates: Linch[51] determined the purity of sodium or potassium xanthate containing sulfites, thiosulfates, sulfides, and thiocarbonates by treating the sample, dissolved in water, with a 10 per cent barium chloride solution. After 2 hours the solution was titrated with 0.1*N* iodine. The method has an accuracy of ±1 per cent, which gives a better assessment of the purity than calculation from the total sulfur content.

Thiourea: An iodometric method in acid medium has been developed for determination of thiourea in the presence of thiocyanate; it was necessary to use very dilute solutions.[52] Skramovsky[53] considers the iodometric method in alkaline solution to be the best of several examined for the determination of thiourea.

$$CS(NH_2)_2 + 4NaOI + H_2O \longrightarrow CO(NH_2)_2 + 4NaI + H_2SO_4$$

The formation of a turbidity is due to finely divided sulfur; this might be avoided by changing the order of the iodine and alkali addition.

Procedure: To the solution containing about 0.02 g. of thiourea add 25 ml. of 0.1*N* iodine solution and 5–10 ml. of 10 per cent potassium hydroxide solution. Set aside for at least 10 minutes. Acidify with 5–10 ml. of approximately 12 per cent hydrochloric acid and titrate the excess of iodine with thiosulfate solution.

Compounds Containing the Sulfhydryl Group: Compounds which contain the sulfhydryl group usually react with iodine to form the corresponding disulfide compound:

$$2RSH + I_2 \longrightarrow RSSR + 2HI$$

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[51] A. L. Linch, *Anal. Chem.*, 23, 294 (1951).

[52] J. E. Reynolds and E. A. Werner, *J. Chem. Soc.*, 83, 1 (1903).

[53] S. Škramovský, *Chem. Zentr.*, 1941, II, 379.

The reaction has been applied to the determination of thioglycolic acid, cysteine, glutathione, and alkyl mercaptans and indirectly to the determination of acrylonitrile and α,β-unsaturated aldehydes and of several metals after precipitation with thionalide. The procedures are best considered individually.

Thioglycolic Acid: According to Klason and Carlson,[54] thioglycolic acid is quantitatively oxidized by iodine to dithioglycolic acid:

$$CH_2SHCOOH + I_2 \longrightarrow (SCH_2COOH)_2 + 2HI$$

Mayr and Gebauer[55] showed that thioglycolic acid solutions were rapidly oxidized by air. They dissolved the acid in air-free water and added this from a burette to the standard iodine solution until the latter was bleached. The accuracy of the procedure was about 0.5 per cent (cf. p. 391).

Cysteine: Cysteine is oxidized to cystine by iodine and can be titrated in the same way as thioglycolic acid. Bickford and Schoetzow[56] found that side reactions could occur in aqueous solutions and recommended the use of alcoholic solutions. At the end-point the alcohol content must be at least 80 per cent.

Procedure: Dissolve 0.2–0.3 g. of cysteine hydrochloride in 100 ml. of absolute ethanol and titrate with 0.1*N* aqueous iodine solution until the yellow color remains permanent for 30 seconds. Deduct 0.05 ml. of 0.1*N* solution as a correction.

Note: A thorough study of the influence of various factors (temperature, acidity, water content at the end-point, etc.) would be desirable.

Glutathione: King and Lucas[57] state that glutathione can be directly titrated with iodine if the pH of the solution lies between 1.0 and 5.0. At higher pH or at temperatures above 25°C., too much iodine is consumed.

The method has been much used in biochemical analysis. Initially, the end-point was determined by external indicators; sodium nitroprusside gave the best results.[58] Although it was claimed that starch gave good results,[59] others reported that the use of starch as an external indicator did not give sharp end-points and the results were 40–60 per cent higher than those obtained with sodium nitroprusside. The addition of potassium iodide to the mixture, however, stabilized the color produced by starch with iodine and permitted the use of starch as an internal indicator.[60] The presence of iodide in the reaction mixture also permitted the use of potassium iodate[61] as titrant instead of iodine. This method has been used for the determination of cysteine.[62] All these factors were taken into consideration by Woodward and Fry [63] when they developed their widely used iodometric method. Any iodometric titration also determines ascorbic acid (cf. p. 401) and it is therefore necessary to correct for this compound; this may be achieved by titration with dichlorophenol-indophenol and making an appropriate correction or by destroying the ascorbic acid with ascorbic acid oxidase. Urea, uric acid, creatinine, glucose, fructose, and amino acids other than cysteine do not interfere under the conditions of the determination; thioneine and cysteine are simultaneously titrated. As little as 0.1 mg. of glutathione may be determined by the iodometric titration.[64]

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[54] P. Klason and T. Carlson, *Ber.*, **39**, 732, 740 (1906).

[55] C. Mayr and A. Gebauer, *Z. anal. Chem.*, **113**, 189 (1938).

[56] C. F. Bickford and R. G. Schoetzow, *J. Am. Pharm. Assoc.*, **26**, 409 (1937)

[57] E. J. King and C. C. Lucas, *Biochem. Z.*, **235**, 66 (1931).

[58] C. L. Kennaway and I. Heiger, *Biochem. J.*, **21**, 751 (1927); H. E. Tunnecliff, *ibid.*, **19**, 194 (1925).

[59] J. Uyei, *J. Infectious Diseases*, **39**, 467 (1926).

A method for the separation of glutathione from cysteine by precipitation at different pH with calcium lactate has been described,[65] but the procedure is not completely quantitative.

Water-Insoluble Mercaptans: Mercaptans react with iodine to form the disulfide. Kimball, Kramer, and Reid[66] gave the following procedure.

Procedure: Weigh a sample containing 0.002–0.003 equivalent of mercaptan in a sealed glass ampoule. Place the ampoule in a 250 ml. glass-stoppered Erlenmeyer flask with 50 ml. of $0.1N$ iodine and some glass beads. Shake the flask so that the glass beads break the ampoule and to ensure complete reaction by the free transfer of iodine from the water to the mercaptan layer. Titrate the excess of iodine with thiosulfate in the usual way.

Notes: (1) Water-insoluble mercaptans can also be dissolved in air-free alcohol and titrated with iodine (see the method of Beesing *et al.* below).

(2) Mercaptal and mercaptole derivatives were determined by Holmberg[67] by heating with mercuric chloride in hydrochloric acid solution to cause fission of the sulfide bond. After the addition of potassium iodide, the liberated mercapto acid was titrated with standard iodine solution. Of the compounds examined only the mercaptals of formaldehyde and glyoxal were incompletely decomposed.

Application of the Mercaptan Titration. *Acrylonitrile and α,β-Unsaturated Aldehydes and Esters:* These compounds may be determined by the addition of excess primary mercaptan and determination of the unreacted mercaptan iodometrically or amperometrically.[68]

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[60] H. L. Mason, *J. Biol. Chem.*, 86, 623 (1930); W. A. Perlsweig and G. Delrue, *Biochem. J.*, 21, 1416 (1927).

[61] G. Hunter and B. A. Eagles, *J. Biol. Chem.*, 72, 177 (1927).

[62] Y. Okuda, *J. Biochem.* (*Japan*), 5, 201 (1925).

[63] G. E. Woodward and E. G. Fry, *J. Biol. Chem.*, 97, 465 (1932).

[64] A. Fujita and I. Numata, *Biochem. Z.*, 299, 249 (1939).

[65] L. Binet and G. Weller, *Bull. soc. chim. biol.*, 16, 1284 (1934).

[66] J. W. Kimball, R. L. Kramer, and E. E. Reid, *J. Am. Chem. Soc.*, 43, 1199 (1921).

[67] B. Holmberg, *Arkiv Kemi Mineral. Geol.*, A15, No. 22, 11 pp. (1942).

[68] D. W. Beesing, W. P. Tyler, D. M. Kurtz, and S. A. Harrison, *Anal. Chem.*, 21, 1073 (1949).

The salts of the corresponding acids do not react with the mercaptan under the conditions employed and other unsaturated compounds in general do not interfere.

Reagents. Alcoholic Mercaptan Solution: Dissolve 25 g. of crude *n*-dodecyl mercaptan (dodecanethiol) in 1 liter of ethanol (Formula 2-B) or 2-propanol. *n*-Hexyl mercaptan (hexanethiol) was also tested with satisfactory results and presumably an equivalent quantity of any primary mercaptan may be used, but the commercially available dodecyl mercaptan is a good compromise in solubility and odor. Dilutions of this solution are used for determination of less than 10 mg. of acrylonitrile or other active compound. No secondary or tertiary mercaptans were included in this study.

Basic Catalyst: Dissolve 1 g. of potassium hydroxide in 20 ml. of alcohol or use undiluted Triton B (40 per cent aqueous solution of trimethylbenzylammonium hydroxide).

Standard Iodine Solution: Use 0.05–0.1N iodine solution in aqueous potassium iodide.

Procedure. Pipette 10–50 ml. of alcoholic mercaptan, depending on the optimum excess of mercaptan to be used (see Note 1), into a 125 ml. iodine flask. Weigh into the flask sufficient sample to contain 20–200 mg. of acrylonitrile or other active unsaturated compound. If necessary, neutralize any acidity with base. Add 1 ml. of alcoholic potassium hydroxide or 0.25 ml. (5 drops) of Triton B in excess. Stopper the flask and allow it to stand the optimum time for completion of reaction (see Note 1). Acidify with 1–2 ml. of glacial acetic acid, dilute to about 75 ml. with alcohol, and titrate with iodine solution of appropriate strength to a faint yellow end-point which is permanent for 30 seconds of swirling.

Notes: (1) For acrylonitrile, acrylates, and maleates, the optimum excess or mercaptan is 25–100 per cent and the optimum reaction time is 2 minutes. For methacrylates, crotonates, and aldehydes, the respective figures are 100–150 pe cent and 10–15 minutes; for the semiquantitative estimation of ketones, 200–400 per cent and 20–30 minutes.

(2) If a reaction time of 2 minutes is used, dilute the same volume of mercaptan solution as was used for the experimental determination to about 75 ml. with alcohol and run a blank by direct titration with iodine.

If a longer reaction time is used, run a blank containing the mercaptan and the basic catalyst through the entire procedure and also run a direct blank titration of mercaptan with no base. The difference between these blank values represents the error due to air-oxidation of mercaptan in the basic solution. A part of this error proportional to the amount of excess mercaptan present in the experimental run must be subtracted from the direct titration blank. Because the greater part of the active compound reacts with mercaptan within 2 minutes, this method of blank correction is satisfactory. Alternatively, oxygen may be swept from the alcoholic mercaptan with an inert gas before addition of sample or basic catalyst.

$$\%\ \text{active compound} = \frac{(B - A)N \times E \times 100}{W}$$

where A = ml. of iodine required for the unknown, B = ml. of iodine required for the direct mercaptan blank (corrected if necessary), N = normality of iodine, E = milliequivalent weight of reactive compound, and W = weight of sample.

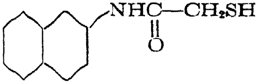
Thioglycolic-β-aminonaphthalide (Thionalide).

Determination of Different Metals with Thionalide: It has long been known that thioglycolic acid in mineral acid solution forms complexes with various metals. If the carboxyl group is transformed to the anilide, the thioglycolic acid anilide, $C_6H_5NHCOCH_2SH$, forms more stable complexes. The complex formation must be traced to the SH group, the hydrogen of which can be replaced by metals. Berg and Roebling[69] have found that thionalide ($C_{10}H_{17}NH—CO—CH_2SH$) yields very insoluble complexes with various metals (see Table I).

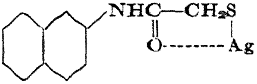
TABLE I

Sensitivity of the Precipitation with Thionalide in 0.2*N* Sulfuric Acid Solution

Metal	Sensitivity (mg./liter)	Metal	Sensitivity (mg./liter)
Cu	0.1	As	0.01
Ag	0.2	Sb	0.02
Au	0.4	Bi	0.1
Hg	0.06	Pt	0.1
Sn	0.08	Pd	0.1



Thionalide



Silver thionalide

In addition to precipitations from mineral acid solutions, numerous metals, such as cadmium, lead, nickel, cobalt, manganese, and thallium, precipitate from acetic acid, neutral, or alcoholic solutions. Gold, thallium, tin, lead, antimony, and bismuth in solutions containing tartrate and potassium cyanide form stable and insoluble complexes. In ammoniacal tartrate solution, however, only thallium precipitates as a lemon-yellow crystalline precipitate.

Thionalide is odorless, white, or delicately ivory colored and crystallizes in needles (m.p. 111–112°C.). It is slightly soluble in water (0.01 per cent at 20°C.) but easily soluble in acetic acid or alcohol.

Thionalide can be titrated directly with iodine using starch as indicator.

Precipitation with thionalide in mineral acid solution has been found especially valuable for the determination of *copper, silver, mercury, and bismuth.*

Reagent: A freshly prepared 1 per cent solution in alcohol or glacial acetic acid. In order to eliminate a possible dissolution effect of the solvent on the metallic complex, the amount of organic solvent used is controlled so that it forms about 10–15 per cent of the solution after the precipitation.

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[69] R. Berg and W. Roebling, *Ber.*, 68, 403 (1935); *Z. angew. Chem.*, 48, 430 (1935).

General Procedure. Heat the mineral acid solution to boiling and precipitate with the reagent solution. Filter through paper which has been moistened with hot water, wash the precipitate, and transfer it with the paper to a beaker. Add methanol and dilute sulfuric acid and titrate with 0.02*N* iodine, using starch as indicator.

Note: Oxidizing substances and trivalent iron must be reduced before the determination because they oxidize the reagent; this is best done with hydroxylamine sulfate.

Details for the determination and separation of various metals have been given by Berg and Roebling.[70]

Copper: The general procedure is used; the amount of reagent added should be about 10 times the expected amount of copper; e.g., for 0.02 g. of copper in 150 ml., use 20 ml. of 1 per cent reagent solution. Precipitation can be done from sulfuric or nitric acid solution; the acidity should be less than 0.5*N*. Chloride up to 1 g. per 100 ml. has no effect on the precipitation in slightly acid (0.1*N*) solution, but larger chloride concentrations cause low results while higher acidities cause high results. After being washed, the precipitate is transferred to the original beaker and dissolved in 50 ml. of glacial acetic acid and 4–5 ml. of 5*N* sulfuric acid; 0.1 g. of potassium iodide, 10 ml. of 1*N* thiocyanate, and excess of 0.02*N* iodine are added and, after dilution with water, the excess of iodine is titrated with 0.02*N* thiosulfate with starch as indicator. A solution of potassium iodate can be used instead of iodine. One milliliter of 0.02*N* iodine corresponds to 1.272 mg. of copper.

Interfering ions can be removed before the determination. Ferric iron is reduced with hydroxylamine sulfate. Large amounts of chloride are removed by fuming with sulfuric or nitric acid. The excess of reagent in the filtrate is recovered by adding approximately 0.5*N* potassium iodide–iodine solution at 70–80°C. while stirring until a yellow color appears. After cooling the insoluble "dithionalide" is filtered off.

Silver: Silver is determined in the same way as copper but the addition of thiocyanate is omitted. Lead and cadmium do not interfere.

Mercury: This is determined in the same way as silver. Greater than 0.1*N* chloride concentrations cause high results. If mercuric nitrate is to be analyzed, it is converted to mercuric chloride by addition of chloride. A three-fold excess of the reagent should be used for the precipitation.

Bismuth: The complex can be precipitated from sulfuric or nitric acid solutions. It is unfilterable at first but becomes crystalline after 20–30 minutes digestion on a water bath. The acid concentration must not exceed 0.1*N*, but under these conditions basic bismuth salts precipitate on warming; therefore the precipitation is done in the presence of 0.2*N* mineral acid and the solution is neutralized to 0.1*N* acid immediately afterwards with sodium hydroxide. The intense yellow precipitate has the formula $Bi(C_{12}H_{10}ONS_3) \cdot H_2O$. If more than 1 per cent of sodium chloride is present, the bismuth is partly complexed and escapes determination.

For the iodometric determination of the precipitate, ammonium chloride is added to decompose the bismuth iodide, in such an amount that the solution is permanently saturated. One milliliter of 0.02*N* iodine corresponds to 1.393 mg. of bismuth.

If much lead is present, this is precipitated from a large volume (200–400 ml.) at a nitric acid concentration of not less than 0.1*N*.

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[70] R. Berg and W. Roebling, *Z. angew. Chem.*, 48, 597 (1935).

Thallium: Berg and Fahrenkamp[71] found that under suitable conditions the determination of thallium as thionalide permits a separation form silver, copper, gold, platinum, palladium, tungsten, molybdenum, lead, mercury, bismuth, cadmium, arsenic, antimony, tin, vanadium, zinc, iron, cobalt, nickel, chromium, aluminium, uranium, and the alkali and alkaline earth metals.

Reagent: A freshly prepared solution of 5 per cent of thionalide in acetone. This solution is only stable for some hours.

General Procedure. To the thallium solution add 10–25 ml. of 20 per cent sodium tartrate solution for each 100 ml. of total volume and neutralize to phenolphthalein with $2N$ sodium hydroxide. Add 20 per cent potassium cyanide so that about 5 per cent of potassium cyanide will be present in the final solution. Add $2N$ sodium hydroxide to raise the alkalinity to about N concentration (5 per cent potassium cyanide corresponds to an alkalinity of $0.75N$; 0.55 g. of iron consumes 4 g. of cyanide. The remaining 1 g. of cyanide gives the solution an alkalinity of $0.15N$). Precipitate the thallium at room temperature with a four- to five-fold excess of reagent solution (for 100 mg. of thallium, about 0.4–0.5 g. of thionalide in 8–10 ml.). Heat to boiling with gentle stirring; the precipitate coagulates and then becomes vivid yellow and crystalline. Cool, filter, wash the cyanide out with cold water, and rinse with 2–3 ml. portions of acetone until thionalide is no longer detectable in the filtrate. (To test, dilute 2–3 times with water; acidify with sulfuric acid; after some drops of N iodine solution have been added, there should be no turbidity or opalescence.) Transfer the precipitate and filter to the precipitation vessel and treat with a mixture of 3 parts of glacial acetic acid to 1 part of $2N$ sulfuric acid. Add an excess of $0.02N$ iodine solution and back-titrate with $0.02N$ thiosulfate, using starch as indicator. One milliliter of $0.02N$ thiosulfate corresponds to 4.09 mg. of thallium.

Notes: (1) The method gives satisfactory results in presence of Ag, Cu, As, Sb, Sn, W, Mo, Zn, Al, Co, Ni, and Fe(II). Trivalent iron, vanadate, and higher oxidation states of gold, platinum, and palladium must be reduced with hydroxylamine salts. In presence of cadmium, more cyanide must be added (for 0.2 g. of cadmium about 7–9 per cent final concentration of potassium cyanide). Uranyl can partially coprecipitate as sodium uranate with the thallium. Before the washing, the sodium uranate can be extracted with 10 per cent ammonium carbonate solution.

(2) Gold, thallium, tin, lead, bismuth, and antimony are quantitatively precipitated by thionalide from solutions containing sodium carbonate, tartrate, and cyanide. Berg and Fahrenkamp[72] have used this method for gravimetric determination of lead, and antimony in the presence of many other metals. Probably the washed precipitates could also be determined iodometrically. This has been done satisfactorily in the case of lead.[73]

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[71] R. Berg and E. S. Fahrenkamp, *Z. anal. Chem.*, **109**, 305 (1937).

[72] R. Berg and E. S. Fahrenkamp, *Z. anal. Chem.*, **112**, 161 (1938).

[73] C. Cimerman and M. Ariel, *Anal. Chim. Acta*, **12**, 13 (1955).

(3) An indirect method for the determination of rhodium with thionalide has been suggested.[74]

7. Hydroxy Compounds. ***Resorcinol:*** Willard and Wooten[75] determined resorcinol iodometrically.

$$C_6H_4(OH)_2 + 3I_2 \longrightarrow C_6HI_3(OH)_2 + 3HI$$

Very few of the common phenols interfere. *m*-Dihydroxyphenols (phloroglucinol and orcinol) also absorb iodine and interfere; *o*-dihydroxyphenols (catechol) interfere by forming very dark flocculent precipitates which obscure the end-point. Catechol, however, may be removed by the lead acetate method of Jones *et al.*[76]

Buffer: To 120 ml. of glacial acetic acid dissolved in about 1700 ml. of water add concentrated sodium hydroxide solution until the pH is about 4.5. Cool to room temperature and continue the neutralization with dilute sodium hydroxide until the pH is 5.0. Store in a rubber-stoppered bottle and check the pH periodically.

Procedure: Dissolve the sample, containing about 0.05 g. of resorcinol, in a little water and add 50 ml. of buffer. Add 50 ml. of $0.1N$ iodine solution from a pipette. After 1 minute titrate the excess of iodine with $0.1N$ sodium thiosulfate in the presence of starch indicator.

Notes: (1) At pH 2 low results were obtained; at pH 4.5 with a reaction time of 2–6 minutes the results were satisfactory. However, at pH 5 satisfactory results were obtained after 30 seconds. The reaction should not be allowed to proceed for much more than 60 seconds.

(2) Hydroquinone interferes but the effect may be overcome by strongly acidifying with hydrochloric acid after the iodination period.

(3) Samples containing 50 mg. of resorcinol may be determined with an error of less than 5 parts per 1000, and samples of 1 mg. with an error of less than 10 parts per 1000.

Phenolphthalein: Phenolphthalein may be determined by iodinating in an alkaline medium to tetraiodophenolphthalein.[77]

$$C_{20}H_{14}O_4 + 4I_2 + 6NaOH \longrightarrow C_{20}H_8I_4O_4Na_2 + 4NaI + 6H_2O$$

Procedure: To an aqueous alkaline solution containing about 50 mg. of phenolphthalein add 20 ml. of $0.1N$ iodine, set aside for 2 hours, acidify with sulfuric acid while cooling, and titrate the excess of iodine with sodium thiosulfate solution.

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[74] J. Kienitz and L. Rombock, *Z. anal. Chem.*, **117**, 241 (1939).

[75] H. H. Willard and L. A. Wooten, *Anal. Chem.*, **22**, 585, 759 (1950).

[76] D. O. Jones, M. A. Prahl, and J. R. Taylor, *Ind. Eng. Chem., Anal. Ed.*, **4**, 84 (1932).

[77] A. Lespagnol and Y. Quevenne, *Pharmacie-Prod. pharm.*, **2**, 98 (1944); through *J. Am. Pharm. Assoc.*, **35**, 298 (1946).

Notes: (1) Lactose and honey interfere.
(2) Recoveries of 99–100 per cent were obtained.
(3) Gravimetric procedures in which the tetraiodophenolphthalein is isolated and weighed or the phenolphthalein is transformed to the oxime by treating with hydroxylamine hydrochloride were also developed.

Warren *et al.*[78] determined phenolphthalein similarly in mineral oil emulsions. Substances which react with iodine (principally glycerin) were removed by means of a slightly acid solution of sodium chloride which broke up the emulsion.

Procedure: Pour approximately 10 ml. of the mineral oil emulsion into a 125 ml. separatory funnel from a tared, glass-stoppered weighing bottle. Determine the weight of sample by difference. Add 30 ml. of 25 per cent sodium chloride solution containing 0.25 per cent of hydrochloric acid to the separatory funnel and shake the mixture continuously for 5 minutes. Allow the mixture to separate and draw off the lower aqueous layer onto a 12.5 cm. filter paper which has been wetted with distilled water and which contains 1 g. of Hyflo Super Cel. Repeat the extraction with 30 ml. of the sodium chloride solution and then with four successive 20 ml. portions, in each case the aqueous layer being filtered through the Hyflo Super Cel. Discard the clear filtrate. Finally wash the filter paper with two 20 ml. portions of the sodium chloride solution and place in a 500 ml. glass-stoppered Erlenmeyer flask. Add 30 ml. of N sodium hydroxide solution to the material in the separatory funnel and shake for 1 minute. Transfer the contents of the separatory funnel to the 500 ml. flask containing the filter paper. Rinse the separatory funnel quantitatively with a total of about 50 ml. of distilled water. The total volume of liquid in the flask should not exceed 125 ml. Add 50 ml. of $0.1N$ iodine solution from a burette. Stopper the flask and shake occasionally until the pink color has been discharged and the mixture assumes a white color with a greenish yellow tint. Add 15 ml. of hydrochloric acid to the flask and titrate the excess of liberated iodine immediately with $0.1N$ sodium thiosulfate solution, using starch as indicator. Prepare a blank by adding to a 500 ml. glass-stoppered Erlenmeyer flask the following: 30 ml. of N sodium hydroxide solution, 15 ml. of hydrochloric acid, 75 ml. of distilled water, one 12.5 cm. filter paper, 1 g. of Hyflo Super Cel, and 25 ml. of $0.1N$ iodine solution.

One milliliter of $0.1N$ thiosulfate corresponds to 3.979 mg. of phenolphthalein.

Hydroquinone: Under suitable conditions, hydroquinone can be quantitatively oxidized to quinone by iodine:

$$C_6H_4(OH)_2 + I_2 \rightleftharpoons C_6H_4O_2 + 2I^- + 2H^+$$

The reaction is reversible and is wholly comparable with the reversible oxidation of arsenious trioxide by iodine or the reduction of arsenic acid by hydriodic acid.

From the equation above, the relationship

$$\frac{[\text{Hydr}][I_2]}{[\text{Quin}][I^-]^2\,[H^+]^2} = K$$

is obtained, where Hydr = hydroquinone and Quin = quinone. From the normal potentials for both systems, Kolthoff[79] calculated

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[78] A. T. Warren, J. E. Logun, and R. L. Thatcher, *J. Am. Pharm. Assoc.*, **39**, 10 (1950).

[79] I. M. Kolthoff, *Rec. trav. chim.*, **45**, 745 (1926).

$K = 5 \times 10^2$. Valeur[80] has recommended the direct titration of hydroquinone in bicarbonate solution using starch as indicator. The addition of an excess of iodine to the bicarbonate solution and back-titration with thiosulfate has also been recommended,[81] but on principle this is not wholly satisfactory because under these conditions a small part of the thiosulfate is oxidized to sulfate (p. 213); with a small excess of iodine, the error would only be very small. The titration, if made in a solution of too low pH, is inaccurate because the concentration of triiodide in equilibrium with the iodide and quinone at the equivalence point is appreciable.[79] However, if the titration is made at a pH of the order of 8 to 9 there are other sources of error: (*a*) the hydroquinone is readily oxidized by oxygen of the air, and (*b*) the quinone may undergo disproportionation reactions to form orange- to black-colored products which interfere with the detection of the iodine starch end-point and which may also involve reaction with iodine. Moreover, the solution must not have a pH greater than about 10 because the reaction

$$I_3^- + 2OH^- = IO^- + 2I^- + H_2O$$

then causes an appreciable error.

Procedure:[79] To 25 ml. of about $0.05M$ hydroquinone, add 0.1–1 ml. of $4N$ acetic acid, 20 ml. of $2N$ sodium acetate, and an excess of $0.1N$ iodine. Set aside for 3 minutes and then back-titrate with thiosulfate.

Notes: (1) The accuracy of this titration is 0.3 per cent. Even with $0.001N$ solutions, an accuracy of 1 per cent can be achieved.

(2) The small amount of acetic acid must be added before the acetate to prevent some of the hydroquinone being oxidized to quinone by air in alkaline solution.

The procedure which involves back-titration with thiosulfate in a bicarbonate medium gives results which are about 0.8 per cent high. If arsenite is used for the back-titration, the accuracy is similar to that of the above method.[82]

Procedure: Weigh a sample of 0.15–0.2 g. and transfer it to an Erlenmeyer flask. Add 25 ml. of water, dissolve the hydroquinone, and add 5 g. of solid carbon dioxide and 2 g. of sodium hydrogen carbonate. Cover the flask with a small watch glass and swirl the flask intermittently until the dry ice has disappeared. Then warm the solution to room temperature but not above. Do not allow the sample to stand any length of time at this point. Add 1 ml. of starch indicator and titrate immediately with $0.1N$ iodine solution to the starch-iodine end-point. Add just 1 ml. of iodine solution in excess and back-titrate with $0.05N$ arsenious acid solution to a light yellow color.

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[80] A. Valeur, *Bull. soc. chim. France*, **23**, 58 (1900).

[81] S. P. L. Sörensen and K. Linderström-Lang, *Compt. rend. trav. lab. Carlsberg*, **14**, No. 14 (1921).

[82] I. M. Kolthoff and T. S. Lee, *Ind. Eng. Chem., Anal. Ed.*, **18**, 452 (1946).

Quinone: A strong acid solution of quinone is quantitatively reduced to hydroquinone by iodide and the equivalent amount of iodine which is liberated can be titrated with thiosulfate. Valeur[83] obtained excellent results in this way. He dissolved the quinone in about 5 ml. of alcohol, added 20 ml. of $4N$ hydrochloric acid and 1.5 g. of potassium iodide, and titrated immediately with thiosulfate.

8. Organic Peroxides. Peroxides in oxidized organic materials are generally determined by reaction with ferrous, iodide, or arsenite ion. The ferrous method, which involves the determination of the ferric ion formed or the excess of ferrous ion remaining after the reduction of peroxides, was studied extensively by Kolthoff and Medalia[84] (cf. p. 186). They showed the significance of the reaction mechanism in the analytical procedure and concluded that the ferrous method is inherently less accurate than the iodometric methods.

(*a*) ***The Iodide Method:*** In the iodide method, the peroxides are reduced by iodide in acid solution and the liberated iodine is titrated with standard thiosulfate solution. Various solvents have been used. Glacial acetic acid or glacial acetic acid with chloroform or carbon tetrachloride is commonly used for the determination of peroxides in fats and oils.[85] Because of the rapid oxidation of iodide by air in this medium, the determination must be carried out in an inert atmosphere. The best results are obtained if the solution of potassium iodide in the solvent is deaerated before the addition of sample. A small amount of water is necessary in the reaction mixture but large amounts retard the reaction of peroxides with iodide. Good results are obtained by using the procedure recommended by Lea.[85]

Procedure: Weigh into the side arm of a special titration flask 1 g. of sample containing about 0.1 meq. of peroxide. Add to the flask 20 ml. of acetic acid-chloroform solvent (3:2 by volume) and 1 ml. of freshly prepared, saturated potassium iodide solution, being careful not to allow these solutions to touch the sample. Deaerate the solvent with nitrogen or carbon dioxide gas. Mix the solution and sample, stopper the flask, and allow it to stand in the dark for 1 hour. Add 30–50 ml. of water and titrate with standard 0.002*N* or 0.01*N* thiosulfate solution.

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[83] A. Valeur, *Compt. rend.*, **129**, 552 (1899).

[84] A. I. Medalia and I. M. Kolthoff, *J. Polymer Sci.*, **4**, 377 (1949); I. M. Kolthoff and A. I. Medalia, *J. Am. Chem. Soc.*, **71**, 3777, 3784, 3789 (1949); *Anal. Chem.*, **23**, 595 (1951).

[85] H. A. Liebhafsky and W. H. Sharkey, *J. Am. Chem. Soc.*, **62**, 190 (1940); C. H. Lea, *Proc. Royal Soc.* (*London*), **108B**, 175 (1931); *J. Soc. Chem. Ind.*, **65**, 286 (1946); D. H. Wheeler, *Oil & Soap*, **9**, 89 (1932).

Notes: (1) Instead of the solution being allowed to stand for 1 hour for complete reaction, the mixture can be heated to boiling for 30 seconds, cooled in a 77° bath for 2 minutes, cooled under tap water, diluted with water, and titrated with thiosulfate.

(2) Nozaki[86] reported that acetic anhydride which does not contain much acetic acid is an excellent solvent for the iodometric determination of organic peroxides. The iodide-peroxide reaction in this medium is rapid and no precaution against oxygen is necessary. Hartman and White,[87] on the other hand, obtained high and erratic blanks with acetic anhydride as solvent and recommend the use of a solvent containing 2 g. of citric acid, 12 ml. of tertiary butyl alcohol, and 7 ml. of carbon tetrachloride in the Lea procedure to reduce the blank titration. The peroxides are reduced completely by iodide within 15 minutes in this medium.

(3) Sully[88] used an air-free atmosphere; he boiled the solvent (1:1 by volume acetic acid–chloroform mixture) in a flask fitted with an air condenser reflux tube topped by a water condenser. When the solvent is refluxing steadily an aqueous solution of potassium iodide is added slowly enough to maintain constant refluxing and the solution is boiled for 3 to 5 minutes, cooled rapidly, diluted with water, and titrated with standard thiosulfate.

The use of alcohol as solvent reduces the air-oxidation of iodide but the peroxide-iodide reaction in this medium is also slow and it is necessary to heat the mixture. Kokatnur and Jelling[89] give the following procedure for the determination of small amounts of organic peroxides.

Procedure: Dissolve the sample in 99 per cent isopropanol (usually 25–50 ml.). Add 1 ml. of saturated potassium iodide solution and 1 ml. of glacial acetic acid. Heat the mixture almost to boiling and keep *at incipient boiling* for 2 to 5 minutes with occasional swirling. Without cooling, titrate the solution with standard sodium thiosulfate solution to the disappearance of the yellow color.

Notes: 1. With reasonable precaution, loss of iodine by volatilization is less than 1 per cent. Vigorous boiling for 5 minutes may result in appreciable losses. Longer incipient boiling beyond that necessary to reduce the peroxide has no effect on the results.

(2) Water retards the peroxide-iodide reaction; if it is present, it may be necessary to heat longer than 5 minutes. Reheating may be used as a check on the analysis. Radford[90] found that the presence of as much as 17 per cent water did not affect the determination of benzoyl peroxide by this method.

[86] K. Nozaki, *Ind. Eng. Chem., Anal. Ed.*, 18, 583 (1946).

[87] L. Hartman and M. D. L. White, *Anal. Chem.*, 24, 527 (1952).

[88] B. D. Sully, *Analyst*, 79, 86 (1954).

[89] V. R. Kokatnur and M. Jelling, *J. Am. Chem. Soc.*, 63, 1432 (1941).

[90] A. J. Radford, *Analyst*, 79, 501 (1954).

Wagner, Smith, and Peters[91] modified the method of Kokatnur and Jelling[89] by using sodium iodide, which is more soluble in the reaction mixture than potassium iodide, eliminating water from the reaction mixture, and using a reflux condenser to avoid loss of iodine.

Procedure: To a 250 ml. Erlenmeyer flask, add 40 ml. of anhydrous isopropyl alcohol, 2 ml. of glacial acetic acid, and up to 10 ml. of sample containing up to 2 meq. of peroxide. Attach a reflux condenser to the flask, heat the solution to reflux, add through the condenser 10 ml. of isopropyl alcohol saturated with sodium iodide, and continue heating to gentle reflux for 5 minutes. Disconnect the condenser, add 5 ml. of water, and titrate the solution with standard thiosulfate to the disappearance of the yellow color.

Notes: (1) Under the conditions of the method, iodine does not add to monoolefins. In the absence of peroxides, iodine does not add to diolefins, but results on diolefin peroxides vary widely with changes in experimental conditions, indicating that these peroxides are not determined accurately by this method. In the analysis of conjugated diolefin samples of low peroxide content, air must be excluded.

(2) The reaction of thiosulfate with triiodide is slow unless 5–10 per cent of water is present in the reaction mixture. Normally this water is supplied by the thiosulfate solution but, if the titer is small, water must be added.

Greenspan and MacKellar[92] determine hydrogen peroxide and aliphatic peroxy acids in the presence of one another by titrating the hydrogen peroxide in a dilute sulfuric acid solution at 0–10°C. with ceric sulfate, then titrating the peroxy acid iodometrically. Diacyl peroxides react only very slowly with iodide under these conditions and do not interfere. These peroxides may be determined iodometrically by heating the resultant solution on a steam bath for 10 minutes and titrating with thiosulfate solution.

Dialkyl peroxides are not determined by any of the procedures given above. More drastic conditions must be used for these peroxides.[93]

(*b*) ***The Arsenite Method:*** For the determination of benzoyl peroxide in organic solvents, Siggia[94] used a standard arsenite solution to reduce the peroxide. Complete solution of the organic material was effected by the addition of ethanol or of benzene and ethanol. After the peroxide was completely reduced and the organic solvent removed by boiling, the excess of arsenite was back-titrated with standard iodine solution.

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[91] C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, **19**, 976 (1947).

[92] F. P. Greenspan and D. G. MacKellar, *Anal. Chem.*, **20**, 1061 (1948).

[93] F. H. Dickey, J. H. Raley, F. F. Rust, R. S. Tresede, and W. E. Vaughan, *Ind. Eng. Chem.*, **41**, 1673 (1949).

[94] S. Siggia, *Anal. Chem.*, **19**, 872 (1947).

Procedure: To 25 ml. of 0.1*N* sodium arsenite (containing 25 g. of sodium bicarbonate per liter) add sufficient material to yield 0.005–0.010 g. of active oxygen. If the sample is immiscible with water, add ethanol until a homogeneous solution is obtained. If the sample is a polymer, dissolve it in benzene and add the ethanol as before. Precipitation of the polymer does not affect the results appreciably. However, if the peroxide content of the polymer is greater than 5 per cent of benzoyl peroxide, pour off the supernatant liquid from the precipitate, redissolve the polymer, and reprecipitate it with ethanol; then combine the extracts.

Add boiling chips and concentrate the solution to about 25 ml. while a stream of air flows over the liquid to increase the rate of evaporation. Add water to give a volume of about 40 ml. Continue this procedure until practically all the monomer and alcohol, or other organic solvent, are replaced by water. Then just acidify the solution with *N* sulfuric acid and add 0.5 g. of sodium bicarbonate. Chill the solution and titrate the excess of arsenious oxide with standard 0.05–0.1*N* iodine to the appearance of yellow iodine color.

Notes: (1) Large amounts of organic solvent in the water cause the end-point to appear slowly; it is sharp if these are removed.

(2) No interference was noted from unsaturated compounds when iodine was added to the excess of arsenite because the latter reacts instantaneously. Moreover, repeated boiling with water removes most of the organic material which might interfere.

(3) The method is sufficiently sensitive to allow 0.008 g. of active oxygen to be determined to within ±0.5 per cent.

(4) Walker and Conway[95] modified the procedure for the determination of peroxides in petroleum products. Aqueous arsenite solution is used to reduce the peroxide in a two-phase system; complete reaction is ensured by prolonged refluxing in an atmosphere of nitrogen. The aqueous phase is separated from the oil phase and back-titrated with standard iodine solution. Good results are obtained with pure hydroperoxide solutions; results for hydroperoxides in gasoline and fuel oil, which often contain iodine-consuming compounds, are thought to be better than those obtained by the iodide method; however, the procedure is tedious and complicated to carry out.

9. Miscellaneous Compounds. *Tetraethyl Lead:* An alcoholic solution of tetraethyl lead can be directly titrated with iodine:

$$R_4Pb + I_2 \longrightarrow R_3PbI + RI$$

The reaction is slow toward the end but is promoted by methanol and chloroform. Hein, Klein, and Mesée[96] give the following method.

Procedure: Add 5 ml. of methanol to 5 ml. of the alcoholic tetraethyl lead solution and titrate with 0.05–0.1*N* alcoholic iodine solution until the yellow color persists for at least 15 minutes.

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[95] D. C. Walker and H. S. Conway, *Anal. Chem.*, 25, 923 (1953).

[96] F. Hein, A. Klein, and H. J. Mesée, *Z. anal. Chem.*, 115, 177 (1939).

Note: Newman *et al.*[97] determine tetraethyl lead in aviation gasoline by shaking with an excess of alcoholic potassium triiodide solution; the interferences of olefins and aromatic amines are minimized, if necessary, by previous extraction with 70 per cent (by volume) sulfuric acid. The excess iodine is titrated with sodium thiosulfate. The method requires about 15 minutes for two concurrent determinations on the same fuel and is applicable to all aviation gasolines that are in current use.

Triethyl Lead: A solution in methanol is titrated with a solution of iodine in methanol:

$$2(C_2H_5)_3Pb + I_2 \longrightarrow 2(C_2H_5)_3PbI$$

The titration of tetraphenyl lead is more involved.

Isonicotinic Acid Hydrazide: This compound reacts with iodine as follows:

$$2RCONHNH_2 + 2I_2 \longrightarrow RCONHNHCOR + N_2 + 4HI$$

Haugas and Mitchell[98] compared the bromometric and iodometric methods; they concluded that the former gives higher results with the pure compound, but when tablets are analyzed the iodometric method also gives high values because of the excipient present (cf. p. 534).

Procedure: Dissolve 0.5 g. in water, dilute to 250 ml. in a volumetric flask, and transfer 25 ml. to an iodine flask. Add 1 g. of sodium bicarbonate, 25 ml. of water, 25 ml. of $0.1N$ iodine, stopper the flask, and set aside for 15 minutes. Add 10 ml. of $5N$ hydrochloric acid and titrate with $0.05N$ thiosulfate.

Notes: (1) Lactose interferes in this procedure but not in the bromometric method.

(2) Struszyński and Bellen[99] prefer to oxidize with iodate and to titrate the excess iodometrically.

Ascorbic Acid (cf. p. 626): Stevens[100] determined ascorbic acid in fruit juices iodometrically but recommended a double back-titration to improve the end-point. He stated that the interference of other reducing substances is minimized by proper adjustment of the acidity. At high acidities the reaction is said to be more specific.

Procedure: To 20 ml. of the fruit juice add 4 ml. of $12N$ sulfuric acid (the pH should be about 0.02–0.08). Add an excess (1–2 ml.) of $0.01N$ iodine solution and after 30 seconds add 3 ml. of 0.5 per cent starch solution and $0.01N$ thiosulfate until there is about 1 ml. in excess. Titrate with $0.01N$ iodine.

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[97] L. Newman, J. F. Philip, and A. R. Jensen, *Anal. Chem.*, 19, 451 (1947).

[98] E. A. Haugas and B. W. Mitchell, *J. Pharm. Pharmacol.*, 4, 687 (1952); cf. T. Canbäck, *ibid.*, 407.

[99] M. Struszyński and Z. Bellen, *Przemysl. Chem.*, 32, 40 (1953).

[100] J. W. Stevens, *Ind. Eng. Chem., Anal. Ed.*, 10, 269 (1938); cf. K. Backe-Hansen and A. Nordal, *Dansk Tidsskr. Farm.*, 28, 53 (1954)

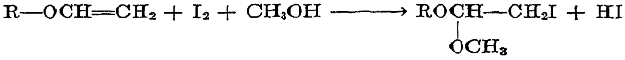
One milliliter of $0.01N$ iodine corresponds to 0.88 mg. of ascorbic acid.

Notes: (1) Iron(II) and tin(II) (from the container) interfere.

(2) Rosenthaler[101] reacted ascorbic acid with mercuric chloride and determined the mercurous chloride so produced either gravimetrically or iodometrically.

(3) Pimenta[102] adds an excess of $0.01N$ potassium iodate solution and back-titrates. Ballentine[103] prefers to titrate directly with $0.01N$ potassium iodate solution. He treats 5 ml. of juice with 1 ml. of fresh 10 per cent potassium iodide solution and 2 ml. of $2N$ sulfuric acid and then titrates with the $0.01N$ iodate. He claims that the method is more accurate than that of Stevens.

Vinyl Ethers: Siggia and Edsberg[104] recommended an iodometric method for the determination of vinyl ethers; it is necessary to add an alcohol because the end-product of the reaction is the corresponding iodoacetal. The impurities usually associated with vinyl alkyl ether, e.g., alcohols, acetaldehyde, acetals, acetylene, and water, do not interfere.



$$R{-}OCH{=}CH_2 + I_2 + CH_3OH \longrightarrow RO\underset{\substack{|\\ OCH_3}}{CH}{-}CH_2I + HI$$

Procedure: Transfer 50 ml. of methanol to a 500 ml. wide-mouth glass-stoppered bottle. Introduce the sample, sealed in a glass ampoule and containing about 0.001 mole of vinyl ether, into the bottle together with some glass beads. Pipette 50 ml. of $0.1N$ iodine solution into the bottle. Stopper the bottle and grease the stopper, to prevent leaks. Shake so that the beads break the ampoule, and set aside for 10 minutes. Give the bottle an occasional shake during this time. Titrate the excess of iodine with $0.1N$ thiosulfate to the disappearance of the iodine color.

Notes: (1) If the ether is very volatile the bottle must be shaken for the full 10 minutes to ensure complete reaction between the iodine and the vaporized ether.

(2) The iodine color returns, but sufficiently slowly for there to be no interference with the end-point. If the sample is so large that it consumes most of the iodine, the color returns more rapidly and may interfere with the end-point. The amount of sample should be chosen so that only about half the added iodine is consumed. The method is usually accurate to within 0.3 per cent.

Phenylmercuric Nitrate: The iodometric assay of this compound only gives moderate precision, according to Ballard and Suckling.[105]

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[101] L. Rosenthaler, *Z. Vitaminforsch.*, 9, 342 (1939); *Chem. Abstr.*, 34, 2876 (1940).

[102] N. Pimenta, *Chem. Abstr.*, 34, 1345 (1940).

[103] R. Ballentine, *Ind. Eng. Chem., Anal. Ed.*, 13, 89 (1941).

[104] S. Siggia and R. L. Edsberg, *Anal. Chem.*, 20, 762 (1948).

[105] C. W. Ballard and E. J. Suckling, *Pharm. J.*, 154, 67 (1945).

However, Gore and Day[106] state that their modification gives satisfactory results. The reactions are as follows:

$$C_6H_5HgOHC_6H_5HgNO_3 + 2KI \longrightarrow 2C_6H_5HgI + KNO_3 + KOH$$

$$C_6H_5HgI + I_2 \longrightarrow C_6H_5I + HgI_2$$

Procedure: Weigh 0.2–0.3 g. of sample into a dry 500 ml. flask. Add 100 ml. of 70 per cent alcohol and heat to boiling. Maintain the solution at this temperature until dissolution is complete. Remove the flask from the source of heat, add 5 ml. of 10 per cent potassium iodide solution, and mix. Rotate the solution frequently during 10 minutes. Add 5 ml. of acetic acid solution and, while still warm, 25 ml. of $0.1N$ iodine solution. When the precipitate has dissolved, add 300 ml. of water and titrate with $0.01N$ thiosulfate in the presence of starch indicator. Carry out a blank determination.

Uric Acid: In the presence of borax or alkali carbonate, 1 molecule of uric acid readily takes up 2 equivalents of iodine. The titration is done using starch as indicator until the blue color persists for 15 seconds. One milliliter of $0.1N$ iodine corresponds to 8.4 mg. of uric acid. The method is also suitable for the microdetermination of uric acid in urine.[107] The acid is precipitated as ammonium urate, which is titrated iodometrically.

Formation of Periodides. *Antipyrine* ($C_{11}H_{12}N_2O$): Manseau[108] determined antipyrine by adding starch solution to a solution of 1 g. in 100 ml. of water and titrating with iodine solution at 40°C. to the appearance of a blue color. The factor of the iodine solution was determined empirically in the same way with pure antipyrine solution. Kippenberger[109] investigated the quantitative conversion of antipyrine to iodine antipyrine but achieved no great accuracy (3–5 per cent). Bougault[110] examined the iodometric determination of antipyrine very thoroughly. Originally he worked with an alcoholic iodine solution, and Francois[110] obtained usable results by the same method. Later, Bougault[111] himself warned against the use of the alcoholic solution and developed a method with the usual aqueous iodine solution. Kolthoff[112] found this method to be very satisfactory but suggested the following modification.

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[106] D. N. Gore and R. M. Day, *Pharm. J.*, 155, 53 (1945).

[107] P. Wenger, C. Cimerman, and A. Maulbetsch, *Mikrochemie*, 14, 129 (1934); cf. R. Danet, *J. pharm. chim.*, 6, 405 (1927); J. Renaudin, *ibid.*, 15, 109 (1932).

[108] E. Manseau, *Chem. Zentr.*, 1889, II, 561.

[109] C. Kippenberger, *Z. anal. Chem.*, 35, 659 (1898).

[110] J. Bougault, *J. pharm. chim.*, 7, 161 (1898); cf. M. Francois, *ibid.*, 15, 97 (1917).

[111] J. Bougault, *J. pharm. chim.*, 15, 337 (1917).

[112] I. M. Kolthoff, *Pharm. Weekblad*, 60, 194 (1923).

Procedure: To 10 ml. of 1 per cent antipyrine solution add 1.5–2 g. of sodium acetate, 20 ml. of $0.1N$ iodine, stopper the flask, and set aside for 20 minutes. Add 20–25 ml. of ethanol and shake well until all the crystals have dissolved. Titrate the unconsumed iodine with thiosulfate. Instead of ethanol, 10 ml. of chloroform can be added after 20 minutes and the titration with thiosulfate is then carried out with vigorous shaking. The antipyrine is quantitatively converted to iodine antipyrine.

$$C_{11}H_{12}N_2O + I_2 \longrightarrow C_{11}H_{11}N_2OI + HI$$

One milliliter of $0.1N$ iodine corresponds to 9.4 mg. of antipyrine.

Notes: (1) After the addition of iodine, a dark-colored crystalline precipitate is formed which is actually colorless iodine antipyrine with a surface adsorption of iodine.

(2) Salicylate does not interfere in the titration. The method described is therefore suitable for the determination of antipyrine in salipyrine. Caffeine and citric acid also do not interfere, nor do acetanilide, phenacetin, and aspirin, which are often present in medicinal preparations with antipyrine. Pyramidone however, is attacked by iodine.

Theobromine (3,7-dimethylxanthine): According to Emery and Spencer,[113] theobromine in acid solution gives a precipitate of formula $C_7H_8N_4O_2HI_4$ with iodine–potassium iodide. Van Breukeleveen[114] recommended the following method.

Procedure: Dissolve 0.15–0.2 g. of theobromine in 4 ml. of N sodium hydroxide in a 100 ml. volumetric flask and add 50 ml. of $0.1N$ iodine. After 15 minutes, acidify with 15 ml. of $4N$ hydrochloric acid and add 6 g. of sodium chloride. When this has dissolved dilute to the mark with water and filter after 30 minutes. (Reject the first 20 ml. if a paper filter is used.) Titrate an aliquot of the filtrate with thiosulfate solution.

Notes: (1) Caffeine interferes in the determination and must be previously removed with methanol.

(2) Wallrabe[115] found that the Emery-Spencer procedure could be applied satisfactorily to the determination of caffeine and certain of its derivatives.

Atophan (2-phenylcinchoninic acid): Emery[116] describes a method for the iodometric determination of the corresponding sodium salt; this is precipitated from acetic acid solution as the periodide, $(C_6H_{11}NO_2)_2HII_3$, and the unconsumed iodine is back-titrated.

Alkaloids: Alkaloids form periodides of variable composition with iodine-potassium iodide solution. The iodometric titration methods for these vegetable bases are therefore of only slight practical value.[117]

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[113] W. O. Emery and G. C. Spencer, *Ind. Eng. Chem.*, **10**, 605 (1918).

[114] M. van Breukeleveen, *Chem. Weekblad*, **24**, 206 (1927).

[115] G. Wallrabe, *Apoth. Ztg.*, **46**, 341 (1931); cf. A. Jermstad and O. Østby, *Dansk Tiddskr. Farm.*, **7**, 117 (1933).

[116] W. O. Emery, *J. Am. Pharm. Assoc.*, **17**, 18 (1928).

[117] See C. Kippenberger, *Z. anal. Chem.*, **35**, 11, 422 (1896); **39**, 435 (1900); H. Beckurts, *Die Methoden der Massanalyse*, p. 443, where further literature references may be found

Iodine Numbers: The determination of iodine numbers cannot be considered in detail in a text of this nature. The method is well covered in textbooks of oil and fat chemistry. Recently, methods for the determination of iodine (and bromine) numbers have been fully reviewed by Polgár and Jungnickel[118] and this article should be consulted for further details.

Phosgene: Acid-free phosgene is dissolved in acetone, potassium iodide is added, and the liberated iodine is titrated with aqueous thiosulfate solution.[119]

$$COCl_2 + 2KI \longrightarrow CO + 2KCl + I_2$$

The acetone must be free from acid and water, for water reacts with phosgene ($COCl_2 + H_2O \rightarrow CO_2 + 2HCl$) and acid catalyzes the iodination of the acetone. According to Matuszak,[120] it is very difficult to achieve accurate results by the iodometric method and he recommends the following procedure.

Procedure: Absorb the phosgene in a solution of potassium iodide in acetone. The amount of iodide present must be at least several times greater than the amount of iodine liberated. Add an excess of iodate (which will react with any acid and iodide formed) and then an excess of 0.01*N* thiosulfate. After 30 minutes, add water in excess of the acetone present and back-titrate with 0.01*N* aqueous iodine solution. Starch can be used as indicator if the water content of the solution at the end-point is at least 50 per cent.

Nitroso Groups: Diphenylnitrosamine oxidizes iodide in acid solution and liberates an equivalent amount of iodine. Becker and Shaefer[121] have based a method on this reaction.

Procedure: Place the sample in a flask provided with an inlet tube, which is closed by a rubber stopper fitted with an outlet tube. Dissolve the sample in 25 ml. of methanol and add 20 ml. of 5 per cent potassium iodide in 1:1 methanol-water solution. Pass carbon dioxide or nitrogen through the solution for a few minutes and then add 5 ml. of 1:1 hydrochloric acid. After 5 minutes titrate the liberated iodine with standard thiosulfate solution.

Notes: (1) The results obtained were 97.7–99.0 per cent of theoretical.
(2) Nitrosobenzene may be titrated likewise.[122]

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[118] A. Polgár and J. L. Jungnickel, in *Organic Analysis*, Vol. III, Interscience, New York-London, 1956.

[119] Cf. J. C. Olsen, G. E. Ferguson, V. J. Sabetta, and L. Sheflan, *Ind. Eng. Chem., Anal. Ed.*, **3**, 189 (1931).

[120] M. P. Matuszak, *Ind. Eng. Chem., Anal. Ed.*, **6**, 457 (1934).

[121] W. W. Becker and W. E. Shaefer, in *Organic Analysis*, Vol. II, Interscience, New York-London, 1954.

[122] M. M. Lobunets and E. N. Gortins'ka, *Chem. Abstr.*, **35**, 1356 (1941).

Procedure: Dissolve 1 g. of sample in 150 ml. of ethanol in a 250 ml. volumetric flask and dilute to 250 ml. with water. Mix 25 ml. of this solution with 30 ml. of 6*N* hydrochloric acid and 15–20 ml. of 20 per cent potassium iodide solution. After a few minutes titrate with 0.1*N* thiosulfate in the presence of starch indicator.

Cinnamic Acid: When a compound containing the —CHBrCHBr— group is treated with sodium iodide the following reaction occurs:

$$\text{—CHBrCHBr—} + 2\text{NaI} \longrightarrow \text{—CH=CH—} + 2\text{NaBr} + I_2$$

and the iodine liberated can be titrated as a measure of the dibromo group.[123] A common procedure used for the analysis of cinnamic acid is based on the formation of dibromophenylpropionic acid which can be readily purified by extraction and distillation. The iodometric procedure is simpler.

Procedure: Dissolve a few tenths of a gram of cinnamic acid in 10 ml. of ether and add bromine until a persistent yellow color is obtained. Set aside for 24 hours exposed to diffuse light at room temperature. Mix the product with a little water and add a solution of sulfur dioxide until excess of bromine is removed. By means of a separatory funnel, remove the water and evaporate off the ether from the solution in a vacuum. Dissolve the residue in 30 ml. of ethanol, add 5 ml. of 10 per cent sodium iodide in ethanol, and boil for 30 minutes on a water bath under a reflux condenser. Titrate the solution when cold with thiosulfate solution.

Note: The method can be applied to the analysis of mixtures containing esters of cinnamic and benzoic acids, such as the so-called cinnameins, but it is necessary first to saponify the esters by boiling for 30 minutes with a strong solution of potassium hydroxide in ethanol.

***o*-Nitrobenzeneseleninic Acid:** *o*-Nitrobenzeneseleninic acid reacts rapidly and quantitatively with thiosulfate.

$$o\text{-}O_2NC_6H_4Se(O)OH + 3S_2O_3^{2-} + 3H^+ \longrightarrow o\text{-}O_2NC_6H_4SeS_2O_3^- + S_4O_6^{2-} + 2H_2O$$

Foss[124] has based a determination on this reaction.

Procedure: To 12–20 mg. of the acid dissolved in 25 ml. of water, add 5 ml. of 0.1*N* sulfuric acid and then 20–30 ml. of 0.01*N* sodium thiosulfate solution (about 5 ml. in excess). After 2–3 minutes, add starch indicator and back-titrate the excess of thiosulfate with 0.01*N* iodine.

Note: This reaction should be compared with that used in the method for determination of selenious acid (p. 328).

Penicillin: According to Wild,[125] who carried out an extensive investigation of the effect of various factors, the iodometric assay of penicillin gives only "fair to good" results and these are dependent on internal cancellation of errors. The original papers should be consulted for details.

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[123] A. Lespagnol and R. Merville, *Ann. chim. anal.*, 25, 53 (1943).

[124] O. Foss, *J. Am. Chem. Soc* , 70, 421 (1948).

[125] A. M. Wild, *J. Soc. Chem. Ind.*, 67, 90 (1948); cf. J. F. Alicino, *Ind. Eng. Chem., Anal. Ed.*, 18, 619 (1946).

10. Oxidation of Organic Compounds with Potassium Iodate. A fair amount of attention has been devoted to methods for the determination of various organic compounds by oxidation with potassium iodate;[126] the excess of the latter is determined iodometrically or the iodine formed during the oxidation is distilled off and determined. Rosenthaler[127] determined oxalic acid in this way and noted that citric acid did not react; malic and tartaric acids reacted but slightly. He suggested that sodium oxalate might be used as a primary standard in iodometry following his general procedure. Strebinger and Wolfram[128] determined tartaric acid by oxidizing with potassium iodate in a sulfuric acid medium, boiling off the liberated iodine, and titrating the excess of iodate. Tartaric acid was also isolated as the lead salt and then determined by the same procedure. Cuny[129] determined formic, citric, and tartaric acids similarly; the method was also applied to the bismuth and calcium salts of these acids. Acetic acid,[130] glycerin,[131] acetylene,[132] and many xanthyl compounds[133] have also been determined.

Strebinger[134] based a method for the determination of oxygen in organic compounds on oxidation with potassium iodate in concentrated sulfuric acid. If the carbon and hydrogen content of the compound are known it is possible to calculate the oxygen content from the amount of iodate consumed in the reaction. Other investigators have determined carbon and hydrogen which can be calculated from the iodate consumption and the amount of carbon dioxide formed.[135]

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[126] Cf. M. E. Millon, *Ann. chim. phys.*, 13 (3) 29 (1845); W. Hurka, *Mikrochemie*, 31, 83 (1944).

[127] L. Rosenthaler, *Z. anal. Chem.*, 61, 219 (1922); cf. O. Warburg, *Ber.* 58B, 1001 (1925); H. Wieland and F. G. Fischer, *ibid.*, 59B, 1171 (1926); F. G. Fischer and C. Wagner, *ibid.*, 59B, 2384 (1926).

[128] R. Strebinger and J. Wolfram, *Österr. Chem. Ztg.*, 26, 1561 (1923).

[129] L. Cuny, *J. pharm. chim.*, 3, (8) 112 (1926).

[130] W. Hurka, *Mikrochemie*, 30, 228 (1942).

[131] A. Chaumeil, *Bull. soc. chim. France*, 27, 629 (1902); cf. R. Strebinger and J. Streit, *Z. anal. Chem.*, 64, 136 (1924).

[132] R. Strebinger and A. Wojs, *ibid.*, 69, 20 (1926).

[133] L. Cuny and J. Robert, *J. pharm. chim.*, 11 (8) 241 (1930).

[134] R. Strebinger, *Z. anal. Chem.*, 58, 97 (1919); cf. A. Ladenburg, *Ann.*, 135, 1 (1865).

[135] G. Vortmann, *Z. anal. Chem.*, 66, 272 (1925); cf. V. Staněk and T. Nemes, *ibid.*, 95, 244 (1933); R. J. Williams, *J. Am. Chem. Soc.*, 59, 288 (1937); R. J. Williams, E. Rohrman, and B. E. Christensen, *ibid.*, 291; B. E. Christensen and J. F. Facer, *ibid.*, 61, 3001 (1939); B. E. Christensen and R. Wong, *Ind. Eng. Chem., Anal Ed.*, 13, 444 (1941); S. Ohashi, *Bull. Chem. Soc. Japan*, 28, 171 (1955).

CHAPTER IX

DETERMINATION OF WATER WITH KARL FISCHER REAGENT

1. Introduction. The determination of water is one of the most common analytical determinations. Because of its widespread importance, many procedures for the determination involving physical and chemical methods have been developed. Physical methods generally involve separation of the water by oven-drying, absorption, or azeotropic distillation, although measurements of physical properties such as electrical conductivity, dielectric constant, infrared absorption, density, and index of refraction are used for some specific samples. Many chemical reactions, generally involving the hydrolysis of reactive agents such as sodium, hydrides, calcium carbide, magnesium nitride, acetyl chloride, and acetic anhydride, have been suggested. Several acidimetric procedures based on such reactions are described in Vol. II, pp. 210–215.

In 1935 an extremely simple, convenient, and precise method was introduced by Karl Fischer.[1] Water in a sample dispersed in an anhydrous solvent such as methanol is titrated directly with a reagent containing iodine, sulfur dioxide, pyridine, and methanol. The method is reasonably specific for water and is proving to be the most generally applicable of the methods available for its determination. Consequently the use of the reagent is described in an increasing number of publications and is the subject of a complete monograph,[2] to which those interested in a more extended discussion are referred.

2. Stoichiometry of the Reaction. Karl Fischer[1] believed that 1 mole of iodine reacts with 2 moles of water according to the equation:

$$2H_2O + SO_2 + I_2 \longrightarrow H_2SO_4 + 2HI$$

In the presence of pyridine, which is added to combine with the acid products so that this reaction is not reversed, the overall reaction is expressed by the equation

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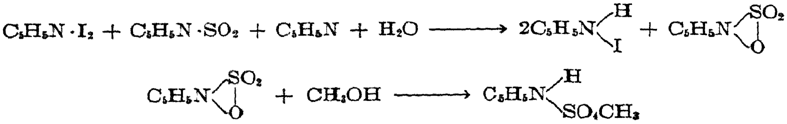
[1] K. Fischer, *Angew. Chem.*, **48**, 394 (1935).

[2] J. Mitchell, Jr., and D. M. Smith, *Aquametry. Application of the Karl Fischer Reagent to Quantitative Analyses Involving Water*, Interscience, New York-London, 1948.

$$2H_2O + (C_5H_5N)_2\cdot SO_2 + I_2 + 2C_5H_5N \longrightarrow (C_5H_5N)_2\cdot H_2SO_4 + 2C_5H_5N\cdot HI$$

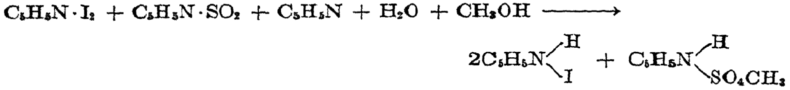
In a more thorough investigation of the stoichiometry of the reaction, Smith, Bryant, and Mitchell[3] found that 1 mole of iodine reacts with only 1 mole of water in the presence of pyridine and methanol. The reaction was shown to take place in two distinct steps, water being involved in the first step only:



$$C_5H_5N\cdot I_2 + C_5H_5N\cdot SO_2 + C_5H_5N + H_2O \longrightarrow 2C_5H_5N\left\langle\begin{matrix}H\\I\end{matrix}\right. + C_5H_5N\left\langle\begin{matrix}SO_2\\|\\O\end{matrix}\right.$$

$$C_5H_5N\left\langle\begin{matrix}SO_2\\|\\O\end{matrix}\right. + CH_3OH \longrightarrow C_5H_5N\left\langle\begin{matrix}H\\SO_4CH_3\end{matrix}\right.$$

The overall reaction which takes place is given by the equation:

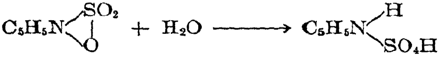


$$C_5H_5N\cdot I_2 + C_5H_5N\cdot SO_2 + C_5H_5N + H_2O + CH_3OH \longrightarrow 2C_5H_5N\left\langle\begin{matrix}H\\I\end{matrix}\right. + C_5H_5N\left\langle\begin{matrix}H\\SO_4CH_3\end{matrix}\right.$$

Each mole of water requires 1 mole of iodine, 1 mole of sulfur dioxide, 3 moles of pyridine, and 1 mole of methanol.

Using a modified Fischer reagent to avoid the decomposition and hygroscopicity of the usual solution, Johansson[4] and Seaman, McComas, and Allen[5] confirmed the observation that 1 mole of iodine reacts with only 1 mole of water.

In the absence of methanol and in the presence of excess water it is possible to replace methanol in the second step with water:



$$C_5H_5N\left\langle\begin{matrix}SO_2\\|\\O\end{matrix}\right. + H_2O \longrightarrow C_5H_5N\left\langle\begin{matrix}H\\SO_4H\end{matrix}\right.$$

so that 2 moles of water react with 1 mole of iodine; however, in the presence of excess methanol, the intermediate compound reacts preferentially with methanol. Titrations in the absence of methanol are of little practical importance since the reaction is then not specific for water. Any active hydrogen compound can react with the intermediate compound and upset the stoichiometry of the reaction. In addition, a reagent prepared without methanol quickly deteriorates, and the end-point of the titration is not so sharply and clearly defined.

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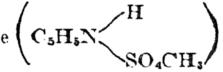
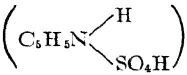
[3] D. M. Smith, W. M. D. Bryant, and J. Mitchell, Jr., *J. Am. Chem. Soc.*, 61, 2407 (1939).

[4] A. Johansson, *Svensk Papperstidn.*, 50, No. 11B, 124 (1947); *Chem. Abstr.*, 41, 7116 (1947); *Acta Chem. Scand.*, 3, 1058 (1949).

[5] W. Seaman, W. H. McComas, and G. A. Allen, *Anal. Chem.*, 21, 510 (1949).

3. Preparation and Stability of Karl Fischer Reagent. ***Composition:*** According to the stoichiometric requirements of the reaction between water and Karl Fischer reagent, 1 mole of water requires 1 mole of iodine, 1 mole of sulfur dioxide, 3 moles of pyridine, and 1 mole of methanol. The reagent used by Fischer[1] contained an excess of sulfur dioxide, pyridine, and methanol so that the iodine concentration was the limiting factor in the strength of the reagent. His solution contained the components in the ratio: 1 mole I_2:3 moles SO_2:10 moles C_5H_5N:120 moles CH_3OH. The pyridine is necessary to combine with the acid products formed by the reaction. In addition, the pyridine combines with iodine and sulfur dioxide to reduce their vapor pressure and thus makes the reagent more stable. Iodine and sulfur dioxide act like acids in the G. N. Lewis sense to form "neutralization products" with the base pyridine. The excess methanol also serves several functions. Being an active hydrogen compound, it reacts with the intermediate compound, pyridine sulfur trioxide, rendering it inactive toward water. Methanol is a good solvent for the various products of the reaction which, if insoluble, interfere with the reaction end-point. Finally, the methanol helps to stabilize the reagent to some extent.

The Fischer reagent was investigated thoroughly by Smith, Bryant, and Mitchell[3] in an effort to identify the compounds present in active and spent mixtures. The study indicated that the active components in the reagent exist principally as the binary compounds: pyridine diiodide ($C_5H_5N \cdot I_2$) and pyridine sulfur dioxide ($C_5H_5N \cdot SO_2$) along with some pyridine hydroperiodide ($C_5H_5N\text{-}HI_2$). No ternary compounds were isolated or observed. In the spent reagent, the principal components observed were pyridine hydroiodide ($C_5H_5N\text{-}HI$) and pyridine hydrogen methyl sulfate  $\left(C_5H_5N\begin{matrix}\diagup H\\ \diagdown SO_4CH_3\end{matrix}\right)$ along with some pyridine hydrogen sulfate  $\left(C_5H_5N\begin{matrix}\diagup H\\ \diagdown SO_4H\end{matrix}\right)$.

Numerous preparations of Karl Fischer reagent have been described. It has been found that a good general purpose reagent should have the components in approximately the ratio 1 mole I_2:3 moles SO_2:10 moles C_5H_5N diluted with methanol so that 1 ml. of the resulting reagent reacts with 3 to 6 mg. of water. Most of the preparations suggested in the literature have this general composition.[6]

For various special purposes the composition may be altered. For example, in the determination of water in alcohols only 4–5 moles of pyridine per mole of iodine may be used. On the other hand, higher concentrations of pyridine may be desirable for the determination of water in acetone to inhibit acetal formation. A reagent solution equivalent to only 1 mg. of water per milliliter may be used for the determination of traces of water. Reagent solutions of this strength have been observed to be slightly more stable than those more concentrated.

The presence of water in the chemicals used in the preparation of Karl Fischer reagent decreases its strength by an equivalent amount. The water content of the solvents used in the reagent preparation, therefore, should not exceed 0.1 per cent. Reagent grade solvents which are sufficiently anhydrous are commercially available. However, anhydrous methanol is hygroscopic enough to require care in handling and storage and should be tested for water content if it has been exposed to moisture.

Stability: Freshly prepared Karl Fischer reagent shows a marked decrease in strength within the first 2–3 days followed by a more gradual decrease with time.[3] After the first week the strength decreases about 1 per cent per day. The freshly prepared solution, therefore, should be allowed to stand at least 24 hours before being standardized and should be restandardized periodically (at least once each day it is used). It has been observed that freshly prepared reagent generally has about 80 per cent of its theoretical strength and that this decreases to about 50 per cent after 1 month and to about 40 per cent after 3 months. Part of the initial loss in strength comes from the moisture content of the chemicals, but part is most likely caused by side reactions. The gradual decrease in strength is due primarily to the latter. If the solution is not adequately protected from moisture in the air, the rate of decrease is accelerated. Smith, Bryant, and Mitchell, in their study of the nature of the side reactions, observed that these do not involve the iodination of pyridine, as had been assumed, but rather a reduction of iodine to iodide and the formation of quaternary methylpyridinium salts, probably:

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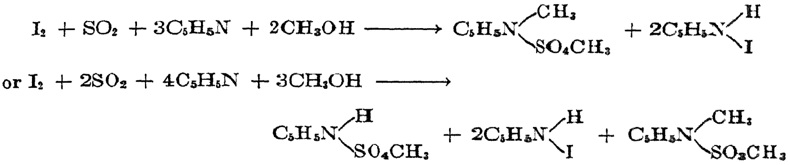
[6] C. Ricciuti and C. O. Willits, *J. Assoc. Offic. Agr. Chemists*, **33**, 469 (1950).



$$I_2 + SO_2 + 3C_5H_5N + 2CH_3OH \longrightarrow C_5H_5N\begin{array}{l} \diagup CH_3 \\ \diagdown SO_4CH_3 \end{array} + 2C_5H_5N\begin{array}{l} \diagup H \\ \diagdown I \end{array}$$

$$\text{or } I_2 + 2SO_2 + 4C_5H_5N + 3CH_3OH \longrightarrow$$

$$C_5H_5N\begin{array}{l} \diagup H \\ \diagdown SO_4CH_3 \end{array} + 2C_5H_5N\begin{array}{l} \diagup H \\ \diagdown I \end{array} + C_5H_5N\begin{array}{l} \diagup CH_3 \\ \diagdown SO_3CH_3 \end{array}$$

No way has been found to prevent these reactions. However, this has not been a serious handicap since the reagent solution is easily standardized before use. After the freshly prepared reagent has aged for a few days, daily standardizations are usually sufficient. According to Blomgren and Jenner,[7] the reagent can be made more stable by adding to it some of the decomposition product to maintain equilibrium.

Temperature does not markedly influence the decomposition of the reagent. Nevertheless, the reagent is probably photosensitive since a solution allowed to stand in a burette for long periods of time becomes weaker than the solution in the reservoir.

Karl Fischer reagent prepared without methanol decomposes very quickly. On the other hand, reagent prepared without sulfur dioxide is practically completely stable. Reagent containing all components except sulfur dioxide has the added advantage that it is less hygroscopic than the complete reagent. It is convenient, therefore, to prepare stable "stock" solutions containing no sulfur dioxide, to which sulfur dioxide may be added a few days before the reagent solution is needed. Several preparations based on this scheme have been proposed.

Preparation of Fischer Reagent: Smith, Bryant, and Mitchell[8] suggested the preparation of a stock solution containing iodine, pyridine, and methanol. The stock solution is chilled in ice and liquid sulfur dioxide is added carefully several days before the reagent solution is needed. Almy, Griffin, and Wilcox[8] recommended a solution containing pyridine and sulfur dioxide, to which methanol and iodine are added several days before the reagent is needed. Commercially available Karl Fischer reagent generally consists of two stock solutions, one of iodine in methanol and the other of sulfur dioxide in pyridine. These solutions are mixed several days before use. Wiberley[9] suggested the addition of methanol to the sulfur dioxide-pyridine solution.

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[7] E. Blomgren and H. Jenner, Brit. Pat. 722,983 (December 9, 1952).

[8] E. G. Almy, W. E. Griffin, and C. S. Wilcox, *Ind. Eng. Chem., Anal. Ed.*, 12, 392 (1940).

Procedure of Smith, Bryant, and Mitchell: Transfer 84.7 g. (0.33 mole) of resublimed iodine to a dry 1 liter glass-stoppered bottle and add 269 ml. (3.3 moles) of reagent grade pyridine containing less than 0.1 per cent water (e.g., Eastman Chemical No. 214-H). Shake the mixture until the iodine is completely dissolved and add 667 ml. of anhydrous methanol containing less than 0.05 per cent water. The resulting stock solution is stable and may be kept almost indefinitely. Several days before the reagent is required, cool the stock solution in an ice bath. Collect 64 g. (44.5 ml., 1 mole) of anhydrous liquid sulfur dioxide in a cold trap immersed in a solid carbon dioxide bath and protected from atmospheric moisture. Carefully add the sulfur dioxide to the chilled stock solution, keeping the solution mixed by shaking. Stopper the mixture, allow it to return to room temperature, and keep it for several days before using. The resulting reagent should be equivalent to about 3.5 mg. of water per milliliter.

Notes: (1) Since the order of the mixing of the chemicals does not influence the strength or stability of the prepared reagent, advantage is taken of the more rapid dissolution of iodine in pyridine than in methanol.

(2) Considerable heat is liberated when sulfur dioxide is added to the stock solution. By chilling the solution in an ice bath before adding sulfur dioxide, and adding the latter in liquid form, the heating effect can be conveniently controlled.

(3) The method of preparation may be modified somewhat to yield equally good reagent solutions. Almy, Griffin, and Wilcox[8] suggested the following variation: Weigh 3.785 liters (1 gal.) of pyridine into a flask and add 755 g. of liquid sulfur dioxide. This stock solution may be stored in a glass-stoppered bottle. Several days before use, the complete solution is prepared by transferring 1359 g. of stock solution to a 5 liter bottle. Add 1786 g. (2.25 liters) of methanol, mix, cool to room temperature, and add 453.6 g. (1 lb.) of iodine. Stopper and cool the bottle; then alternately swirl and cool the solution until the iodine is completely dissolved. The proportions of the constituents in the resulting solution are 1 mole I_2:2 moles SO_2:8 moles C_5H_5N, and the solution is equivalent to about 5.3 mg. of water per milliliter.

(4) For microtitrations, Wiberley[9] suggested the preparation of two solutions as follows:

Solution 1: Add 50 g. of resublimed iodine to a freshly opened 1 lb. bottle of anhydrous methanol, stopper, and allow to stand until the iodine completely dissolves.

Solution 2: Place 2 lb. of anhydrous methanol and 160 ml. of anhydrous pyridine in a 2 liter screw-cap bottle. Cool the solution in an ice bath and carefully add 28 ml. of anhydrous liquid sulfur dioxide. To prepare the complete reagent several days before it is required mix 145 ml. of Solution 1 and 330 ml. of Solution 2. The proportions of the components in the resulting solution are 1 mole I_2:3 moles SO_2:10 moles C_5H_5N, and the solution is equivalent to about 1 mg. of water per milliliter.

Modified Reagents: Smith, Bryant, and Mitchell[3] studied the possibility of substituting other organic nitrogen bases for pyridine and other inert solvents for methanol in Karl Fischer reagent.

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[9] J. S. Wiberley, *Anal. Chem.*, 23, 656 (1951).

Bases other than pyridine may be used but this is not advantageous. The following bases were compared with pyridine: aniline, dimethylaniline, quinoline, tri-*n*-butylamine, and triethanolamine. Fischer reagents prepared with aniline, dimethylaniline, and triethanolamine were very unstable; the solution prepared with aniline decomposed almost completely within 24 hours. Quinoline and tri-*n*-butylamine closely parallel pyridine, although more tri-*n*-butylamine seems to be required in the reaction than is the case for pyridine; almost 4 rather than 3 moles of base are required per mole of water.

Several solvents were substituted for methanol: benzene, dioxane, glacial acetic acid, ethanol, acetonitrile, dimethylformamide, and pyridine. Most of these solvents are not so satisfactory as methanol since the amine salts which are products of the reaction with water are less soluble in them than in methanol. This is especially true of benzene and dioxane, and less so for ethanol, acetonitrile, and glacial acetic acid. Dimethylformamide and pyridine are satisfactory with regard to solubility, but Fischer reagent prepared without methanol tends to be less stable than solution containing methanol.

Bonauguri and Seniga[10] noted that the titer varied with the age of the reagent, being slightly high with fresh reagent and low with old reagent. They suggest a reagent consisting of iodine, sulfur dioxide, pyridine, and methanol in the proportion of 1:2:9:16 and recommend that dioxane dehydrated over sodium be used in place of methanol for diluting the sample. They claim that better results are thus obtained.

Peters and Jungnickel[11] recommend methyl Cellosolve in place of methanol, and decrease the amount of solvent so that the effective strength of the reagent is three times as great as the original Karl Fischer reagent. The reagent is more stable, of wider application, and less subject to interfering side reactions. A mixture of ethylene glycol and pyridine (4:1) is recommended as solvent for the sample, particularly when ketones are present. Better end-points are obtained than in a methanolic solvent and it is not necessary to convert the ketone to the cyanohydrin. Large amounts of the lower aldehydes (except formaldehyde) interfere, however, and must be converted to cyanohydrins. The possible interference of organic acids is eliminated.

Ethylene glycol is also recommended for extracting water from hydrocarbons and concentrating it in a small volume. The extraction and titration are carried out in a special flask, the titration being done in the presence of the extracted hydrocarbon.

Some fifty other reactions were examined by Belcher and West[12] to find an alternative reagent, but very few were suitable. A reagent containing cupric chloride, sulfur dioxide, pyridine, and methanol showed some promise:

$$2CuCl_2 + SO_2 + 2H_2O \longrightarrow Cu_2Cl_2 + 2HCl + H_2SO_4$$

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[10] E. Bonauguri and G. Seniga, *Z. anal. Chem.*, 144, 161 (1955).

[11] E. D. Peters and J. L. Jungnickel, *Anal. Chem.*, 27, 450 (1955).

[12] R. Belcher and T. S. West, *J. Chem. Soc.*, 1772 (1953); T. S. West, Ph.D. Thesis, Birmingham University, 1953.

and gave good visual and potentiometric end-points, but it deteriorated so rapidly that it was useless for practical purposes. The only reagent which was comparable with the Karl Fischer reagent was one in which bromine was used in place of iodine, but methanol could not be used as solvent because it reacted vigorously with the other components. The bromine reagent has some advantages over the original Karl Fischer reagent as regards stability, visual detection of end-points, and stoichiometry, but these are outweighed by its greater reactivity toward alcohols which necessitates their complete absence from the system being titrated. Titrations can be made either visually or potentiometrically, as with the Karl Fischer reagent, or by adding a known excess to a pyridine solution of water, destroying this excess with anhydrous ethanol and then determining the acid produced by titration with standard alkali in the usual way.

Johansson's Two-Reagent Modification: An unique modification of the Karl Fischer reagent was introduced by Johansson[4] and further studied by Seaman, McComas, and Allen.[5] Two solutions were used instead of the usual Karl Fischer reagent in order to avoid decomposition and minimize hygroscopicity. The sample was dispersed in a solution of sulfur dioxide, pyridine, and methanol, then titrated with a solution of iodine in methanol. These two solutions when mixed constitute Karl Fischer reagent and react rapidly and stoichiometrically with water. Alone, however, each is more stable and less hygroscopic than Karl Fischer reagent. The iodine solution may be conveniently standardized by thiosulfate titration or by other conventional methods for iodine. When this is done the water present in the two solutions contributes a constant correction to the determination of water in the sample. Seaman, McComas, and Allen[5] therefore found it more convenient to standardize the iodine solution empirically by titrating a standard water sample. Because the iodine solution in methanol is stable it need not be standardized as frequently as regular Fischer reagent. The modified titration is as precise and as widely applicable as the usual Karl Fischer titration.

If an excess of iodine solution is added to the sample and back-titrated with standard water solution in methanol, the initial, very rapid decomposition observed for freshly prepared Karl Fischer reagent can cause difficulties. If a slight excess (e.g., 5–10 ml.) of iodine solution (equivalent to 2 mg. of water per milliliter) is added to 25 ml. of the sulfur dioxide and pyridine solution in methanol and immediately back-titrated, the decomposition amounts to only 2–3 per cent. However, if the mixture is allowed to stand for 3 minutes before it is back-titrated, the decomposition may amount to about 25 per cent. With a larger excess of iodine solution (more than 20 ml.) the decomposition amounts to about 25 per cent for back-titration both immediately and after a 3 minute interval. The rate of decomposition is greatly reduced by chilling the reaction mixture in an ice-salt bath. The back-titration method can be used if the reaction mixture is kept at −10° to −15°C. with no more than 10 ml. of excess iodine solution present and if the reaction mixture is not allowed to stand longer than 10 minutes before being back-titrated. The decomposition error is not observed if a direct titration rather than a back-titration method is used.

Reagents: (A) Add 190 g. of liquid sulfur dioxide to 950 ml. of ice-cold anhydrous methanol in a 2-liter bottle. Mix the solution and add 950 ml. of anhydrous pyridine, slowly at first. In the preparation of this reagent it is convenient to weigh the sulfur dioxide first and then adjust the volumes of methanol and pyridine so that 5 ml. of each will be present per gram of sulfur dioxide.

(B) Dissolve 60 g. of resublimed iodine in 2 liters of anhydrous methanol. The solution is equivalent to about 2 mg. of water per milliliter.

Notes: (1) Reagent B shows very small changes in strength with age, according to the data of Seaman, McComas, and Allen:[5]

Time (days)	0	3	7	14	21	28
Effective H_2O equiv. (mg. H_2O/ml.)	1.985	1.966	1.953	1.952	1.937[a]	1.907

[a] Between the 14th and 21st days the drying tube was off for a period not exceeding 15 hours.

Reagent A exhibits an apparent decrease in moisture content on standing. Seaman and his coworkers titrated equal portions of this solution with standard iodine in methanol, after the following intervals:

Time (days)	0	3	4	5	6	10	13	17
Titration, ml.	4.09	3.75	3.40	3.00	2.72	1.10	0.40	0.46

This curious behavior is attributed to air-oxidation of the solution to produce the compound pyridine-sulfur trioxide, which is capable of reacting with water. The reaction does not interfere analytically since a blank titration is always carried out when the sample titration is made.

(2) Johansson[13] suggested a further modification to the two-reagent method for microdeterminations of water. Initial water in the pyridine-sulfur dioxide-methanol solvent (A) is removed by reaction with bromine, with a micro drop of iodine solution (B) as indicator. The sample is then added and titrated with reagent B in the usual way. The hydriodic acid formed is determined iodometrically, essentially as described on p. 249. Since each mole of water yields 2 moles of hydriodic acid, which after conversion to iodate is titrated with 12 equivalents of thiosulfate, this procedure results in a greatly increased titer in the determination of water. However, the actual sensitivity and accuracy of the determination rest upon the accuracy of the original titration of the sample with reagent B, so that no real gain is obtained. Furthermore, any iodide present in reagent B will be titrated the same as though produced by water.

4. Titration Methods. Karl Fischer reagent is a very active desiccant; the apparatus used to store and dispense the reagent, and the titration flask assembly, must be designed to protect the reagent from the moisture in air. The reagent solutions can be used conveniently in all-glass automatic burettes having the solution reservoir and burette in an integral unit which can be protected with drying tubes. These burettes are commercially available in pressure-fill and gravity-fill types. A gravity-fill unit is preferred since less air is introduced through the drying tube during the filling operation. A pressure-type burette may be adapted to vacuum-filling by replacing the pressure bulb with a drying tube and attaching the vacuum system at the top. This adaptation allows a more gradual introduction of air through the drying tube while filling the burette. Most of the common laboratory drying agents can be used to protect the system from moist air.

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[13] A. Johansson, *Acta Chem. Scand.*, 3, 1058 (1949).

The solution being titrated should be protected from exposure to moist air. Bryant, Mitchell, and Smith[14] suggested the use of glass-stoppered volumetric flasks as titration vessels. The long necks on the flasks offer sufficient protection of the solution during a rapid visual titration, yet allow continuous agitation of the solution. Many closed systems in which the titration flask is attached to the burette by ground glass joints, special plastic stoppers, or sheets have been described in the literature.[15] With these closed titration assemblies it is convenient to use a magnetic stirrer to mix the contents of the flask during titration. Several titration assemblies are commercially available.

Solutions used in the Johansson two-reagent modification need not be protected quite so scrupulously as those used in the conventional method because of their decreased hygroscopicity. However, some protection is necessary even with the modified reagent, especially when micro samples are analyzed.

The Fischer determination of water has been adapted to micro titrations;[16] in precision and accuracy they should closely approximate the macro methods. The former have the advantages of greater stability of dilute reagent, smaller size of samples, and lower costs.

End-Point Detection: The end-point of a titration may be detected visually or electrometrically. *Visual titrations* can be made with simpler apparatus and in less time, but require some experience in perceiving the end-point and cannot be used with dark-colored samples. Karl Fischer reagent has the dark brown color of iodine, which is changed to a chromate yellow color by reaction with water. At the end-point the color change from yellow to the reddish brown of unused iodine is sharp and reproducible. As an aid in the detection of this color change it is convenient to prepare one solution having the color of "spent" reagent just before the end-point and another having the color of the iodine end-point. This aid is especially useful to one who is attempting to become familiar with the color change, or is seeking an end-point in the presence of a colored sample. Visual methods are less sensitive than electrometric procedures, but have been used satisfactorily in titrations of water on the milligram scale. The visual end-point may be used in either a direct titration or a back-titration; however, since the back-titration method offers no advantages over the direct but requires the additional water-in-methanol solution, the direct method is generally employed. For routine analyses of large numbers of colorless or lightly colored samples, visual detection of the end-point is often preferred to electrometric methods because of its greater speed and simplicity.

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[14] W. M. D. Bryant, J. Mitchell, Jr., and D. M. Smith, *J. Am. Chem. Soc.*, **62**, 1 (1940).

[15] E. G. Almy, W. E. Griffin, and C. S. Wilcox, *Ind. Eng. Chem., Anal. Ed.*, **12**, 392 (1940); G. Wernimont and F. J. Hopkinson, *ibid.*, **15**, 272 (1943); R. Kieselbach, *ibid.*, **18**, 726 (1946); F. W. Zerban and L. Sattler, *ibid.*, **18**, 138 (1946); G. B. Levy, J. J. Murtaugh, and M. Rosenblatt, *ibid.*, **17**, 193 (1945); J. S. Wiberley, *Anal. Chem.*, **23**, 656 (1951); T. G. Bonner, *Analyst*, **71**, 483 (1946); G. R. Cornish, *Plastics (London)*, **10**, 99 (1946).

[16] G. B. Levy, J. J. Murtaugh, and M. Rosenblatt, *Ind. Eng. Chem., Anal. Ed.*, **17**, 193 (1945); O. T. Aepli and W. S. W. McCarter, *ibid.*, **17**, 316 (1945); M. M. Acker and H. A. Frediani, *ibid.*, **17**, 793 (1945); A. Johansson, *Acta Chem. Scand.*, **3**, 1058 (1949); W. Seaman, W. H. McComas, Jr., and G. A. Allen, *Anal. Chem.*, **21**, 510 (1949); J. S. Wiberley, *ibid.*, **23**, 656 (1951).

Fischer[17] states that the end-point can be readily observed by adding a few drops of methylene blue dissolved in ethanol or pyridine. The change at the end-point is from green to Bordeaux red in transmitted light or dark green in reflected light, and is reversible.

Scott[18] proposed a method by which a visual end-point can be observed in the titration of dark-colored petroleum products. The Fischer reagent is made up with ethanol in place of methanol and the titration is performed in the following manner. Place about 50 ml. of petroleum ether in the titration flask and titrate with the modified reagent until iodine begins to precipitate and adhere to the wall of the flask. Add the weighed sample, shake vigorously, and titrate until iodine again begins to precipitate on the wall of the flask. The amount of reagent used in the second titration corresponds to the water in the sample. By substituting ethanol for methanol, the two-phase liquid system formed during the usual titration is eliminated. In addition, the excess iodine after the end-point, along with reaction and degradation products, is precipitated from the solution and adheres to the wall of the titration flask to give a clearly visible color change.

Electrometric methods used for detecting the end-point are the "dead stop" method of Foulk and Bawden[19] and potentiometric methods based on either a bimetallic system[20] or a platinum electrode with a reference cell. Most commonly the dead stop method is used. The basic electrical circuit for this is shown in Fig. 1.[21] A potential of 10–25 mv. is impressed between two platinum wire electrodes immersed in the titration solution. When iodide but no free iodine is present, the system is polarized and no current flows. When free iodine is added to the solution, the system becomes depolarized and the galvanometer registers a flow of current in the circuit. Wernimont and Hopkinson[19] observed that a direct titration of water sample with Karl Fischer reagent gives a less satisfactory dead stop end-point than does a titration in which an excess of reagent is added to the sample and back-titrated with water-in-methanol solution. In the back-titration, current flows through the galvanometer when the solution contains excess Fischer reagent and drops to zero when the equivalence point is reached.

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[17] E. Fischer, *Angew. Chem.*, 64, 592 (1952).

[18] C. G. Scott, *Analyst*, 76, 237 (1951).

[19] C. W. Foulk and A. T. Bawden, *J. Am. Chem. Soc.*, 48, 2045 (1926); G. Wernimont and F. J. Hopkinson, *Ind. Eng. Chem., Anal. Ed.*, 15, 272 (1943); J. G. van Pelt and H. Keuker, *Chem. Weekblad*, 51, 97 (1955)

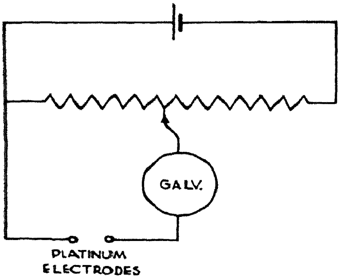

Fig. 1. Conventional "dead stop" apparatus circuit.

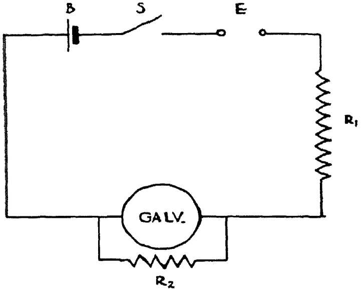

Fig. 2. Modified "dead stop" apparatus circuit.

The dead stop apparatus was modified by Carter and Williamson[22] to adapt the method to direct titration of water samples with Fischer reagent. Their electrical circuit is shown in Fig. 2, where B is a 2 volt cell, S a switch, E the two platinum electrodes, R_1 a 3000–10,000 ohm resistor, G a galvanometer, and R_2 a shunt resistor having resistance 0.025–0.1 times the value of the galvanometer resistance. In their work the galvanometer had a resistance of 373 ohms, a sensitivity of 0.04 microamp. per mm. and a scale of 100 mm.; R_1 was a 5000 ohm resistor, and R_2 a 10 ohm resistor. The resistance of the titration cell changes from more than 15,000 ohms when the electrodes are polarized to around 500 ohms after the end-point when the solution contains iodine and iodide. Since the resistance is in series with the cell, the voltage applied to the electrodes in methanol solution changes from 1 to 2 v. before the end-point to about 0.15 v. after the end-point. This arrangement makes the current change clearly discernible at the end-point of a direct titration.

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[20] J. C. Hostetter and H. S. Roberts, *J. Am. Chem. Soc.*, **41**, 1337 (1919); H. H. Willard and F. Fenwick, *ibid.*, **44**, 2504 (1922); E. G. Almy, W. F. Griffin, and C. S. Wilcox, *Ind. Eng. Chem., Anal. Ed.*, **12**, 392 (1940).

[21] Although electrical methods are not generally discussed in this text, an exception is made here because the electrometric method is so frequently employed in Fischer titrations.

[22] R. J. Carter and L. Williamson, *Analyst*, **70**, 369 (1945).

Electronic instruments based on the dead stop principle have also been suggested for detecting the end-point of the Fischer titration.[23] With these instruments, a small polarizing current is passed through the platinum electrodes in the titration cell and the voltage change across these electrodes is observed with a vacuum tube voltmeter. McKinney and Hall[23] made use of the Serfass titrimeter.[24] The back-titration method was employed by these investigators, but direct titrations with Fischer reagent are also possible.[25] Electronic titrimeters yield sensitive and reproducible end-points and are especially useful for micro titrations.

Many instruments utilizing the dead stop principle are available from laboratory supply houses. These instruments include simple units utilizing microammeters for detecting the end-point, pH meters which are adaptable to Karl Fischer titrations, electronic titrimeters, and completely automatic titrators.

The potentiometric method for detecting the end-point through the use of platinum-tungsten bimetallic electrodes was first applied to the Fischer titration by Almy, Griffin, and Wilcox.[20] The potential change at the end-point is approximately 20 mv. and the electrodes are readily polarized, so that a sensitive millivoltmeter which draws practically no current is necessary. A laboratory pH meter was found to be satisfactory, although any electron tube millivoltmeter may be used. The tungsten electrode must be cleaned and sensitized by dipping the wire in fused sodium nitrate for 5–10 seconds, washing with water, and drying. As in the regular dead stop method, the bimetallic system was found to give a sharper change when water-in-methanol solution was added to the Fischer reagent than when Fischer reagent was added to the water solution.

By using a platinum electrode as the indicator and a glass electrode as the reference electrode, with a pH meter as a potentiometer, Heinemann[26] found no difference in the sharpness of the end-point whether the titration was direct or reverse. However, he did observe more random variations in the determination of water in dairy products by direct titration than by back-titration. This may be due to the rate of extraction of water from these solids coupled with side reactions which occur with Karl Fischer reagent.

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[23] C. D. McKinney, Jr., and R. T. Hall, *Ind. Eng. Chem., Anal. Ed.*, **15**, 460 (1943).

[24] E. J. Serfass, *Ind. Eng. Chem., Anal. Ed.*, **12**, 536 (1940).

[25] M. M. Acker and H. A. Frediani, *Ind. Eng. Chem., Anal. Ed.*, **17**, 793 (1945); R. Kieselbach, *ibid.*, **18**, 726 (1946); *Anal. Chem.*, **21**, 1578 (1949); C. W. Schroeder and J. H. Nair, *ibid.*, **20**, 452 (1948).

[26] B. Heinemann, *J. Dairy Sci.*, **28**, 845 (1945).

5. Standardization of Karl Fischer Reagent. Because of the gradual decomposition of Fischer reagent, it must be standardized empirically at least once each day. This is accomplished readily by titrating a known quantity of water with the reagent. Several methods have been suggested for obtaining standard samples of water; these include the use of a standard solution of water in methanol, pure water dispensed from a weight burette, and stable crystalline hydrates.

The effect of temperature on standardization was studied by Jensen.[27] He states that the titration and standardization must be made at 17–23°C., otherwise an error of greater than 0.1 per cent is obtained. If the temperature of a titration (t_1) deviates from that of the standardization (t_2) the amount of reagent used in the titration should be multiplied by a factor $1 + 0.0012 \times (t_2 - t_1)$.

Standard Water-in-Methanol Solution: This standard was suggested by Fischer as being convenient, reliable, and stable. It can be prepared accurately and can also be used for back-titrations. Solutions commonly used contain approximately 3–15 mg. of water per milliliter. These are prepared directly from water and methanol. Since some water is contained even in "anhydrous" methanol, the moisture content of the solvent must be determined and added to the quantity of water that is weighed.

Procedure: Weigh 2–15 g. of pure water into a dry 1 liter glass-stoppered volumetric flask and dilute to the mark with methanol containing less than 0.1 per cent water.

Direct Titration Method: Titrate several 10 ml. aliquot portions of the anhydrous methanol and several 10 ml. aliquot portions of water-in-methanol solution with Karl Fischer reagent. A 125 ml. Erlenmeyer flask is convenient for each of these titrations. If the flasks are not kept in a desiccator they will adsorb some moisture from the air. Correction can be made for this moisture by adding a small known volume (say 5 ml.) of anhydrous methanol to each of the titration flasks. The volume of Fischer reagent required to titrate the small volume of methanol in a similar titration flask of the same size is subtracted from each of the titers used in the standardization.

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[27] V. G. Jensen, *Dansk Tiddskr. Farm.*, 29, 77 (1955).

The water content of the methanol solution and the water equivalent of the Karl Fischer reagent are then calculated in the following manner: Let

A = grams of water weighed into the volumetric flask.
B = ml. of Fischer reagent required to titrate the small volume of methanol added to correct for adsorbed moisture.
C = ml. of Fischer reagent required to titrate 10 ml. of methanol plus the volume added for adsorbed moisture.
D = ml. of Fischer reagent required to titrate 10 ml. of water-in-methanol solution plus the methanol added for adsorbed moisture.
W = mg. of water per ml. of water-in-methanol solution.
F = mg. of water equivalent to 1 ml. of Fischer reagent.

Thus

$$W = A + \frac{A(C - B)}{D - C} = \frac{A(D - B)}{D - C}$$

and

$$F = \frac{10W}{D - B} = \frac{10A}{D - C}$$

Back-Titration Method:[6] Add 5 ml. of Karl Fischer reagent to a titration flask (to provide an anhydrous atmosphere) and titrate the excess reagent with the water-in-methanol solution. Add a 10–25 ml. (*a* ml.) aliquot portion of Karl Fischer reagent and titrate with water-in-methanol solution (*b* ml.). Add a 10–25 ml. (*c* ml.) aliquot portion of the anhydrous methanol used to prepare the water-in-methanol solution, a known excess (*d* ml.) of Fischer reagent, and titrate the excess with water-in-methanol solution (*e* ml.).

The water content of the water-in-methanol solution and the water equivalent of the Fischer reagent are calculated in the following way: Let A, W, and F have the same significance as in the direct method. Further, let R equal b/a, the number of milliliters of water-in-methanol solution required per milliliter of Fischer reagent. Then

$$W = A + \left(\frac{dR - e}{c}\right) W = \frac{cA}{c + e - dR}$$

$$F = WR$$

Note: The standard water-in-methanol solution is stable over a period of several months, if protected from evaporation, within experimental error. Wernimont and Hopkinson[28] found no change during a 42 day period on a methanol solution containing approximately 5 mg. of water per milliliter.

Other solutions containing water may be used for standardizing the Karl Fischer reagent. Levy, Murtaugh, and Rosenblatt[29] and

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[28] G. Wernimont and F. J. Hopkinson, *Ind. Eng. Chem., Anal. Ed.*, 15, 272 (1943).

[29] G. B. Levy, J. J. Murtaugh, and M. Rosenblatt, *Ind. Eng. Chem., Anal. Ed.*, 17, 193 (1945).

Rulfs[30] used standard ethanol solutions the water content of which was determined from density measurements.

Pure Water as Standard: A logical standard material is water itself, and this is a commonly used, convenient standard. Usually a 10–250 mg. portion of water is added to the titration flask from a weight burette. The procedure for standardization is the same as that used in the analysis of a sample except that water serves as the sample.

Procedures. Direct Titration Method: Add approximately 25 ml. of anhydrous methanol to a titration flask and titrate with Karl Fischer reagent. Weigh a water sample into the flask from a weight burette and titrate with Fischer reagent. The water equivalent of the Fischer reagent, F, is calculated from the volume of reagent used in the second titration.

$$F = \frac{\text{mg. of water used}}{\text{ml. of Fischer reagent used}}$$

Back-Titration Method: Titrate Karl Fischer reagent with water-in-methanol solution to obtain the number of milliliters of water-in-methanol solution required per milliliter of Fischer reagent, R. Add 25 ml. of anhydrous methanol to each of several titration flasks and add weighed samples of water to some. Add 25 ml. of Fischer reagent to each flask and back-titrate with water-in-methanol solution. Both water-in-methanol solution and Karl Fischer reagent are standardized by this procedure:

$$W = \frac{\text{mg. of water used}}{\text{net ml. of water-in-methanol solution used}}$$

$$F = WR$$

Stable Crystalline Hydrates as Standards: Many stable hydrates have been suggested as standard materials. Among those recommended are ammonium oxalate monohydrate,[31] sodium acetate trihydrate,[32] and citric acid monohydrate.[33]

Neuss, O'Brien, and Frediani[34] studied a number of hydrates with the aim of finding one that fulfills the following requirements: (*a*) reagent grade material containing the theoretical amount of water should be commercially available; (*b*) its reaction with Karl Fischer reagent should be rapid and quantitative and should yield a sharp end-point in methanol medium; (*c*) the material should be stable in ordinary containers under varying humidity conditions; and (*d*) the water content should be subject to independent check by a convenient, accurate method, e.g., by loss in weight on heating. Of the hydrates studied, sodium tartrate dihydrate alone was found to possess all the desiderata. The theoretical water content is 15.66 per cent; that found by Karl Fischer titration was 15.65 ± 0.01 per cent, and that by loss in weight at 150°C. 15.65 ± 0.02 per cent. Exposed to air at relative humidities of 20–79 per cent, the hydrate showed a gain in weight of only 0.01–0.09 per cent.

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[30] C. L. Rulfs, *Mikrochemie ver Mikrochim. Acta*, **33**, 338 (1948).

[31] R. P. Rennie and J. L. Monkman, *Can. Chem. Process Inds.*, **29**, 366 (1945).

[32] G. G. Warren, *ibid.*, 29, 370 (1945); L. I. Katzin and J. C. Sullivan, *J. Phys. & Colloid Chem.*, 55, 346 (1951).

[33] G. K. Jones, *Paint Manuf.*, 15, 360 (1945); G. R. Cornish, *Plastics (London)*, **10**, 99 (1946).

[34] J. D. Neuss, M. G. O'Brien, and H. A. Frediani, *Anal. Chem.*, **23**, 1332 (1951).

Sulfosalicylic acid, potassium citrate, and sodium citrate hydrates absorb water at high relative humidity, whereas those of citric acid and sodium acetate not only gain water at high humidity but effloresce at low humidity. These chemicals, if used as standards, should be kept in hygrostats having the proper relative humidities. Ammonium oxalate, ferrous ammonium sulfate, lactose, potassium tartrate, and oxalic acid, although they are not affected by changes in relative humidity, often contain more than the theoretical amount of water. Sodium bitartrate, ferric ammonium sulfate, potassium aluminum sulfate, and potassium sodium tartrate often show less than the theoretical water content.

The standardization procedure is the same as that followed when the Fischer reagent is standardized against weighed samples of water.

Iodometric Standardization: Van der Meulen[35] has described a method of standardization in which the sulfur dioxide and iodine content of the reagent are determined. First the total sulfur dioxide is determined by titrating with standard iodine after adding mercury to combine with free iodine in the reagent; then water is added to a further aliquot to consume the active iodine and its equivalent of sulfur dioxide and the excess of the latter is titrated with standard iodine. The amount of active iodine in the reagent can be calculated from the difference of the two titers.

Procedure: To 5 ml. of reagent add about 1 g. of mercury, shake strongly for 5–10 minutes, and add the mixture to a solution containing 5 g. of potassium iodide dissolved in 5 ml. of water and 25 ml. of glacial acetic acid. Dilute to 50 ml. with water. Pipette a 10 ml. aliquot into 50 ml. of water and determine the sulfur dioxide present with standard $0.1N$ potassium iodate solution using starch indicator.

Add a further 5 ml. of reagent to 70–80 ml. of water in a 100 ml. volumetric flask and dilute to the mark. Take a 20 ml. aliquot, add 50 ml. of water, 5 ml. of $0.5N$ potassium iodide solution, 5 ml. of $5N$ hydrochloric acid, and titrate with $0.1N$ potassium iodate solution using starch indicator.

Standardization by the Two-Reagent Modification: Standardization of the reagent using the Johansson two-reagent modification is carried out like a regular titration, except that the water or hydrate sample is dissolved in the sulfur dioxide-pyridine-methanol solvent and titrated with the iodine-methanol reagent.

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[35] J. H. van der Meulen, *Chem. Weekblad*, **47**, 608 (1951).

Procedure: Pipette 25 ml. of sulfur dioxide-pyridine-methanol solvent solution to a 125 ml. flask and titrate with the iodine-methanol reagent solution. Add a weighed sample of water or sodium tartrate dihydrate to a 25 ml. portion of solvent solution in another flask and titrate with iodine solution. The difference between these two titers is the volume of reagent solution equivalent to the weight of water added.

$$F = \frac{\text{mg. of water added}}{\text{ml. of reagent consumed}}$$

6. Determination of Water in Simple Compounds. ***Organic Compounds:*** The Karl Fischer reagent can be used to determine water in almost all classes of organic compounds. The titration procedure is basically the same as that used in the standardization procedure with known samples of water. Certain substances interfere in the titration: (*a*) by reacting with some component of the Fischer reagent to yield water, e.g., active carbonyl compounds which form acetals with methanol; (*b*) by reducing iodine, e.g., mercaptans which are quantitatively oxidized to disulfides by iodine; (*c*) by oxidizing iodide to iodine, e.g., quinone. Fortunately, the number of interfering organic compounds is quite limited and is further diminished by suitable modifications of the titration procedure. The compounds whose interference cannot be eliminated by such modifications generally react stoichiometrically, so that appropriate corrections can be applied if the amount of interfering substance can be determined by other methods.

Table I summarizes the classes of organic compounds which do not interfere in the usual titration method, those that do not interfere if the procedure is modified, and those that cannot be present without interference.[36]

Compounds having ethylenic and acetylenic bonds do not interfere in the determination of water with Karl Fischer reagent. Fischer[1] made the unexpected observation that a sample of cracked gasoline having an iodine number of 132 was inert to his reagent for determining water. This observation has been confirmed for other unsaturated compounds by other investigators.[37]

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[36] Ref. 2, pp. 106–111.

[37] D. M. Smith, W. M. D. Bryant, and J. Mitchell, Jr., *J. Am. Chem. Soc.*, 61, 2407 (1939); C. D. McKinney, Jr., and R. T. Hall, *Ind. Eng. Chem., Anal. Ed.*, 15, 460 (1943).

TABLE I

Classification of Organic Compounds for Fischer Water Determination

a. Non-interfering Compounds

1. Hydrocarbons: saturated, unsaturated (aliphatic and aromatic).
2. Acids: carboxylic (mono- and poly-), hydroxy, amino, sulfonic.
3. Alcohols: monohydric, polyhydric, phenols.
4. Esters: of carboxylic acids, of inorganic acids, ortho esters, carbamates, lactones.
5. Stable Carbonyl Compounds: sugars, formaldehyde, chloral, diisopropyl ketone, benzil, benzoin.
6. Acetals.
7. Ethers.
8. Acid Anhydrides.
9. Acyl Halides.
10. Nitrogen Compounds: amides, anilides, amines, and amino alcohols (with $K_b \leqq 2.4 \times 10^{-5}$), purines, proteins, lactams, imines, azo and azole compounds, nitriles, cyanohydrins, oximes, hydroxamic acids, amidine salts, isocyanates, cyanic acid derivatives, nitroso and nitro compounds, alkaloids.
11. Halides.
12. Sulfur Compounds: sulfides (thio ethers), disulfides, thiocyanates, isothiocyanates, thio esters, dithiocarbamates, xanthates.
13. Peroxides: hydro-, dialkyl.

b. Compounds Requiring a Modified Procedure

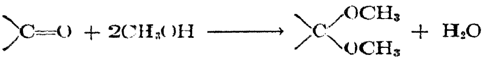
1. Active Carbonyl Compounds.
2. Nitrogen Compounds: amines and amino alcohols (with $K_b > 2.4 \times 10^{-5}$) methylolureas, hydrazine, and substituted hydrazine salts.
3. Sulfur Compounds: mercaptans, thiourea, and *N*-substituted thioureas, thioacids.

c. Interfering Compounds

1. Ascorbic Acid.
2. Quinones.
3. Peroxycarboxylic Acids.
4. Diacyl Peroxides.

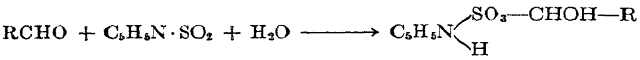
Most organic acids do not interfere in the Fischer titration, yet the readily oxidizable ascorbic acid (vitamin C) is oxidized quantitatively by the iodine in the Fischer reagent. No method is available to inhibit this reaction but, if ascorbic acid can be determined by an independent method, water can be determined by difference.

Active carbonyl compounds interfere in the Fischer titration by reacting with methanol to form acetals or ketals, and water:



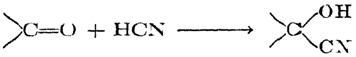
$$\rangle C{=}O + 2CH_3OH \longrightarrow \rangle C\begin{matrix}OCH_3\\ OCH_3\end{matrix} + H_2O$$

This reaction is relatively slow so that carbonyl compounds show themselves by fading end-points in the usual titration procedure. In the presence of the more reactive carbonyl compounds, only a rough approximation of the water content can be obtained. If the Fischer reagent is modified to contain less methanol and more pyridine, a satisfactory titration of water can be made in the presence of ketones but in the presence of aldehydes low results for water are obtained, possibly because of the reaction:



$$RCHO + C_5H_5N\cdot SO_2 + H_2O \longrightarrow C_5H_5N\begin{matrix}SO_3{-}CHOH{-}R\\ H\end{matrix}$$

A better method for overcoming the interference of carbonyl compounds involves transforming them to cyanohydrins with cyanide before titrating the water with Karl Fischer reagent.[38]



$$\rangle C{=}O + HCN \longrightarrow \rangle C\begin{matrix}OH\\ CN\end{matrix}$$

In the presence of sodium or potassium cyanide as catalyst, the reaction proceeds almost completely to the right and, since the resulting cyanohydrins are inert to Fischer reagent, this eliminates the carbonyl interference. Carbonyl compounds which are less reactive with hydrogen cyanide are also practically unreactive with methanol and do not interfere.

Procedure: To a 250 ml. titration flask add 10 ml. of a 1 per cent sodium cyanide solution in methanol and 20 ml. of a 5 per cent hydrogen cyanide solution in dioxane. Add a sample containing less than 30 millimoles of carbonyl and follow with 20 ml. of dry pyridine. Stopper the flask, shake the mixture, allow to stand for 30 minutes at room temperature, and titrate with Karl Fischer reagent. The titration volume, less that obtained for a blank containing 10 ml. of the sodium cyanide solution, 20 ml. of hydrogen cyanide solution, and 20 ml. of pyridine, is equivalent to the water in the sample.

Notes: (1) The solution of sodium cyanide, prepared by dissolving 1 g. of dry sodium cyanide in 100 ml. of dry methanol, may become slightly turbid on standing. This does not affect its activity.

(2) The solution of hydrogen cyanide in dioxane should be prepared in a well-ventilated hood as follows. Collect 70 ml. of liquid hydrogen cyanide in a cold trap at 0–5° and add it to 1 liter of pure anhydrous dioxane in a glass-stoppered

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[38] W. M. D. Bryant, J. Mitchell, Jr., and D. M. Smith, *J. Am. Chem. Soc.*, **62**, 3504 (1940).

bottle cooled in ice. Mix the solution thoroughly, remove from the ice bath, and allow to warm to room temperature. This solution is stable and involves little hazard if stored and used in a well-ventilated hood. Pyridine was originally suggested as an alternative solvent, but the pyridine solution has since been found quite unstable and dioxane is preferred.[39]

(3) The procedure yields good results in the presence of aliphatic and aromatic aldehydes and most ketones. Quinone interferes by oxidizing hydriodic acid (p. 397).

Water in the presence of nitrogen compounds is readily determined by the usual procedure; however, amines, especially those more basic than benzylamine, are preferably dissolved in acetic acid instead of methanol. Hydrazine sulfate does not interfere with the normal Fischer titration, but hydrazine hydrochloride and hydrochlorides of other hydrazine derivatives when dissolved in methanol react mole for mole with the iodine in Karl Fischer reagent. This reaction is inhibited by dissolving the sample in glacial acetic acid instead of in methanol. Two grams of hydrazine salts dissolved in 25 ml. of glacial acetic acid and titrated with Fischer reagent yielded accurate results for the water content.[40] Methylolureas react with the reagent to give very rapidly fading end-points. This interference is avoided by dissolving the sample in dimethylformamide and titrating at −40° C.

Among the organic sulfur compounds, the mercaptans (thiols) are oxidized quantitatively by the iodine in Karl Fischer reagent:[41]

$$2RSH + I_2 \longrightarrow RSSR + 2HI$$

The interference of mercaptans can be eliminated by allowing them to react with an active olefin, such as octene, in the presence of boron trifluoride as catalyst.[42]

$$RSH + R'CH{=}CHR' \longrightarrow R'CH(SR)CH_2R'$$

Procedure: To a 250 ml. glass-stoppered volumetric flask containing 5–10 ml. of glacial acetic acid add the sample containing less than 15 millimoles of mercaptan. Add 10 ml. of boron trifluoride reagent in acetic acid (100 g. BF_3 per liter) or 3 ml. of 45 per cent boron trifluoride reagent in ethyl ether, followed by 6 ml. of octene. Stopper the flask and allow to stand at room temperature for 30 minutes. Add 5 ml. of pyridine carefully and titrate with Karl Fischer reagent. The net titer between this sample and a blank is equivalent to the water content of the sample.

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[39] Ref. 2, p. 153.

[40] Ref. 2, p. 131.

[41] E. C. Milberger, K. Uhrig, H. C. Becker, and H. Levin, *Anal. Chem.*, 21, 1192 (1949).

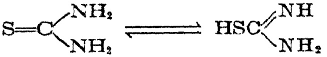
[42] Ref. 2, p. 135–142.

Notes: (1) As catalyst, a boron trifluoride solution in acetic acid or in ethyl ether may be used. The former is prepared by dissolving around 100 g. of anhydrous boron trifluoride in glacial acetic acid to make 1 liter of solution. Ether solutions are commercially available.

(2) Isooctene or mixed octenes may be used as the active olefin.

(3) Alcohols interfere with the method. Methanol and ethanol, especially, esterify acetic acid in the presence of boron trifluoride and yield water. Tertiary alcohols are dehydrated in the presence of boron trifluoride to yield water.

Thiourea and *N*-substituted thioureas in methanol when titrated with Karl Fischer reagent yield fading end-points, indicating reaction with iodine. The reaction may involve tautomerism of the thiourea to isothiourea which then may behave like a mercaptan toward Fischer reagent:



$$S{=}C(NH_2)_2 \rightleftharpoons HSC({=}NH)NH_2$$

thiourea isothiourea

By the procedure as modified for mercaptans, the Fischer titration of water can be made with no interference from thiourea or its derivatives.

Thio acids react quantitatively with the iodine in Fischer reagent. The active olefin-boron trifluoride modification does not improve the situation. However, when an equivalent amount of *n*-butanol is added to a thio acid and the mixture is treated by the olefin-boron trifluoride procedure, the Fischer water titration yields satisfactory results. Exactly the equivalent amount of *n*-butanol must be added, since any excess will esterify the acid to yield water under the conditions of the titration.

Linch[43] used the Karl Fischer reagent to titrate water in xanthate and dithiocarbamate samples dispersed in chloroform. Interference from these substances and their decomposition products was, surprisingly, found to be negligible.

Hydrogen peroxide, organic hydroperoxides, and dialkyl peroxides do not interfere with the normal Karl Fischer titration of water, but diacyl peroxides oxidize hydrogen iodide and so affect the titration values.[44] Hydroperoxides react preferentially with sulfur dioxide.

$$ROOH + SO_2 \longrightarrow RHSO_4$$

Since no water or iodine is involved in the reaction, there is no interference in the titration of water.

Inorganic Compounds. An extensive study of the determination of water in inorganic compounds was made by Bryant and coworkers.[45] Water is determined readily with Karl Fischer reagent. Since many inorganic compounds are relatively insoluble in organic liquids, the titration of water in these compounds is usually carried out with a finely divided suspension of the materials. The following procedure can be used satisfactorily.

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[43] A. L. Linch, *Anal. Chem.*, 23, 293 (1951).

[44] A. Zimmermann, *Fette u. Seifen*, 46, 446 (1939).

[45] W. M. D. Bryant, J. Mitchell, Jr., D. M. Smith, and E. C. Ashby, *J. Am. Chem. Soc.*, 63, 2924, 2927 (1941).

Procedure: Suspend a sample of the finely powdered solid, containing 5–10 millimoles of water, in 25 ml. of methanol (less than 0.1 per cent water) in a 250 ml. glass-stoppered volumetric flask. Titrate with standard Karl Fischer reagent. An end-point stable for 15 minutes usually indicates complete reaction. If the initial titration is incomplete, the mixture may be titrated at 10 minute intervals until a stable end-point is obtained. Run a blank on the methanol. The difference in titer is equivalent to the water content of the sample.

Notes: (1) When the sample is insoluble in methanol, fine grinding is necessary. Methanol, being similar to water, often assists in extracting water from solids by taking the place of water coordinated by the solid. The analysis is expedited further by shaking with a slight excess of Karl Fischer reagent and back-titrating with a standard solution of water in methanol. Ethylene glycol may exert a greater solvent effect and may prove beneficial.

(2) Many inorganic compounds interfere with the determination as discussed below.

Compounds which interfere in the Karl Fischer determination of water are encountered more frequently among inorganic than among organic compounds. Interfering inorganic compounds include: (*a*) oxidizing agents such as peroxides, chromates, cupric, and ferric salts; (*b*) reducing agents such as thiosulfates, and stannous salts; (*c*) compounds which can be considered to form water by reaction with components of Karl Fischer reagent, such as oxides and hydroxides ($MO + 2HI = MI_2 + H_2O$), salts of weak oxyacids ($MSO_3 + C_5H_5N = MO + C_5H_5N{\cdot}SO_2$) and borates ($H_3BO_3 + 3CH_3OH = B(OCH_3)_3 + 3H_2O$). The interfering reactions are often stoichiometric so that frequently corrections may be made for them. In this section inorganic compounds are classified roughly as acids, oxides, peroxides, and salts (including oxidizing and reducing agents) and their effects on the Fischer titration are discussed in that order.

Inorganic acids and acidic oxides generally do not interfere in the determination of water with the Karl Fischer reagent. The reagent has been used successfully for the determination of water in hydrogen fluoride,[46] hydrogen chloride,[41] hydrogen cyanide,[38] nitric, sulfuric, and phosphoric acids,[45] and, of course, hydrogen iodide and sulfur dioxide.[47] The acids are neutralized with pyridine before titrating with Fischer reagent. The gaseous acids can be collected in traps containing pyridine and are then titrated directly.

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[46] C. D. Cook and F. G. Findlater, *J. Soc. Chem. Ind.* (*London*), **66**, 169 (1947).

[47] K. Fischer, *Angew. Chem.*, **48**, 394 (1935); G. V. Zavarov, *Zavodskaya Lab.*, **5**, 1314 (1936); *Chem. Abstr.*, **31**, 2124 (1937); G. A. Lewis, *J. Soc. Chem. Ind. Victoria*, **45**, 576 (1944); B. R. DiCaprio, *Anal. Chem.*, **19**, 1010 (1947).

A few inorganic acids, however, interfere with the determination of water. Hydrogen sulfide reacts quantitatively with the iodine in Karl Fischer reagent.[41] Since the hydrogen sulfide is equivalent mole for mole to water, proper corrections may be made for this interference if the sulfide is determined independently. Boric acid is readily esterified by the methanol in Fischer reagent and, since water is liberated by the reaction, interferes with the determination of water.

$$HBO_2 + 3CH_3OH \longrightarrow B(OCH_3)_3 + 2H_2O$$

$$H_3BO_3 + 3CH_3OH \longrightarrow B(OCH_3)_3 + 3H_2O$$

None of the other inorganic acids is known to form esters in the absence of catalysts.

Inorganic metallic oxides and hydroxides generally react with the hydriodic acid in Fischer reagent to liberate a molecule of water per atom of oxygen in the oxide:

$$MO + 2HI \longrightarrow MI_2 + H_2O$$

$$M(OH)_2 + 2HI \longrightarrow MI_2 + 2H_2O$$

where M represents a divalent metal. The oxides and hydroxides of the alkali and alkaline earth metals react stoichiometrically and without difficulty. In addition the alkali metal salts of weak oxygen acids like carbonic, sulfurous, pyrosulfurous, and arsenious acids may behave like the respective oxides. Typical reactions are illustrated by the following equations:

$$NaOH + HI \longrightarrow NaI + H_2O$$

$$CaO + 2HI \longrightarrow CaI_2 + H_2O$$

$$K_2CO_3 + 2HI \longrightarrow 2KI + CO_2 + H_2O$$

The less basic oxides are less reactive, although copper(I), zinc, silver, and mercury(II) oxides react readily. Aluminum, nickel(II), copper(II), and lead(II) oxides are practically unreactive. The reactivity of these compounds with Karl Fischer reagent probably depends primarily on their solubilities in the titration medium. If a strong anhydrous acid is used to dissolve them, the water may be liberated and titrated quantitatively as a measure of the oxides and hydroxides. Eberius and Kowalski[48] make use of this reaction for the determination of combined oxygen in metals and metallic oxides, a mixture of anhydrous hydrochloric and acetic acids being used as solvent. The method is applicable to all oxides save those of tin, chromium, titanium, and aluminum, which are insoluble in hydrochloric acid.

The weakly acidic oxides, As_2O_3 and B_2O_3, react with Karl Fischer reagent whereas the more strongly acidic oxides do not. Arsenious oxide reacts like the basic oxides forming iodides:[49]

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[48] E. Eberius and W. Kowalski, *Z. Erzbergbau u. Metallhüttenw.*, **7**, 229, 339 (1954).

$$As_2O_3 + 6HI \longrightarrow 2AsI_3 + 3H_2O$$

Boric oxide, like boric acid, shows the unique ester formation:

$$B_2O_3 + 6CH_3OH \longrightarrow 2B(OCH_3)_3 + 3H_2O$$

Silica gel, in spite of its desiccant properties, does not interfere with the Fischer determination of water.

Oxides of metals in higher oxidation states which normally oxidize iodide to iodine may react both as oxidizing agents and as oxides. Since the Fischer titration involves the reaction of 1 mole of water with 1 mole of iodine, the formation of iodine by an oxidation reaction may partly counteract the formation of water by neutralization. Manganese dioxide reacts stoichiometrically.

$$MnO_2 + 4HI \longrightarrow MnI_2 + I_2 + 2H_2O$$

yielding the equivalent of 1 mole of water to be titrated with Karl Fischer reagent. Iron(III) oxide and the lead oxides, PbO_2 and Pb_3O_4, show some reaction but the results are not stoichiometric. Copper(II) oxide, as mentioned above, is practically unreactive. Incomplete reaction is undoubtedly due to insolubilities of the oxides. The lead oxides when heated with glacial acetic acid yield results analogous to that for manganese dioxide.

In order to avoid the interference of sodium hydroxide and other alkaline materials in the determination of water by the Fischer method, Suter[50] separated the water from the alkaline materials by azeotropic distillation with xylene. The method should be fairly generally applicable in the inorganic field.

Procedure: Flush the distillation system free of water by distilling rapidly a few milliliters of xylene. Discard the distillate in the receiving flask and replace the flask. Grind 15–25 g. of the sample with xylene and transfer to the distillation apparatus with additional xylene to make 100 ml. Start the distillation rapidly to sweep the surface moisture over to the receiving flask, cooled in a dry ice-acetone bath. When the distillate comes over clear, cut down the heat and reflux for 4 hours. After the reflux period, distill over the xylene at such a rate that the delivery tube is hot to the receiving flask. Stopper the receiving flask containing the xylene and water, remove it from the dry ice bath and allow it to warm to room temperature. Add 50 ml. of methanol and titrate with Fischer reagent. Correct for a blank titration and calculate the amount of water present.

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[49] It is interesting to note that trivalent arsenic is not oxidized by the iodine in Fischer reagent.

[50] H. R. Suter, *Anal. Chem.*, 19, 326 (1947).

Inorganic peroxides and peroxy salts of noninterfering anions react with Karl Fischer reagent, but moderate quantities do not interfere in the determination of water.[51] Zimmermann,[44] who first reported this interesting observation for hydrogen peroxide, attributed it to the preferential reaction of the hydrogen peroxide with sulfur dioxide rather than with iodide:

$$H_2O_2 + SO_2 \longrightarrow H_2SO_4$$

Since no iodine or water is involved in this reaction it does not interfere with the water determination, provided that a sufficient excess of sulfur dioxide remains.

An extensive study into the determination of water in hydrated salts and water adsorbed on the surfaces of solids was carried out by Bryant *et al.*[45] They found that the ease with which hydrated water is titrated with Karl Fischer reagent depends more on the solubility of the initial or final material in the reaction environment than upon the thermal stability of the hydrate. The use of other inert solvents such as glycol in place of methanol is sometimes beneficial because of increased solvent action. Water was determined successfully in a large variety of hydrated salts of both organic and inorganic acids.

The most frequently encountered interference in the determination of water in salts is that produced by trace impurities of oxides discussed above. In addition, alkali metal salts of weak oxygen acids may react as though they decompose into their component oxides to react with Fischer reagent. Typical reactions are illustrated by the following equations (from which pyridine has been omitted for simplicity):

$$KHCO_3 + I_2 + SO_2 + CH_3OH \longrightarrow KI + HI + CO_2 + HSO_4CH_3$$

$$K_2CO_3 + I_2 + SO_2 + CH_3OH \longrightarrow 2KI + CO_2 + HSO_4CH_3$$

$$NaHSO_3 + I_2 + CH_3OH \longrightarrow NaI + HI + HSO_4CH_3$$

$$Na_2SO_3 + I_2 + CH_3OH \longrightarrow 2NaI + HSO_4CH_3$$

$$Na_2S_2O_5 + I_2 + CH_3OH \longrightarrow 2NaI + SO_2 + HSO_4CH_3$$

$$NaAsO_2 + 2I_2 + 2SO_2 + 2CH_3OH \longrightarrow NaI + AsI_3 + 2HSO_4CH_3$$

$$Na_2B_4O_7 + 7I_2 + 7SO_2 + 19CH_3OH \longrightarrow$$
$$2NaI + 12HI + 4B(OCH_3)_3 + 7HSO_4CH$$

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[51] Ref. 2, pp. 253–255.

Calcium carbonate does not react with Karl Fischer reagent, probably because of its insolubility in methanol. Alkali metal salts of the strong oxygen acids, like the sulfates, acid sulfates, pyrosulfates, dithionites, dithionates and primary and secondary phosphates, are not affected by Fischer reagent. Trisodium phosphate reacts to some extent, probably because of its basic nature.

Strong oxidizing or reducing agents usually interfere by reacting with iodide or iodine. Oxidants cause low results, and reductants high results, in the determination of water. Potentially hazardous oxidants, such as the perchlorates, should not be analyzed by the Fischer method.

Among the cation oxidizing agents, copper(II) salts react quantitatively:

$$CuSO_4 \cdot 5H_2O + 9/2I_2 + 5SO_2 + 5CH_3OH \longrightarrow CuI + 8HI + H_2SO_4 + 5HSO_4CH_3$$

$$CuCl_2 \cdot 2H_2O + 3/2I_2 + 2SO_2 + 2CH_3OH \longrightarrow CuI + 2HCl + 2HI + 2HSO_4CH_3$$

Iron(III) chloride hexahydrate gave a net titer equivalent to 5.60 moles of water, indicating reduction to iron(II):

$$FeCl_3 \cdot 6H_2O + 11/2I_2 + 6SO_2 + 6CH_3OH \longrightarrow FeI_2 + 9HI + 3HCl + 6HSO_4CH_3$$

Laurene,[52] however, was able to overcome this interference by adding a solution of 8–quinolinol dissolved in anhydrous methanol.

Among the anions, arsenite is not oxidized, but arsenate is reduced quantitatively:

$$Na_2HAsO_4 + 3I_2 + 4SO_2 + 4CH_3OH \longrightarrow 2NaI + HI + AsI_3 + 4HSO_4CH_3$$

Sodium nitrite reacts stoichiometrically:

$$NaNO_2 + {}^1/_2I_2 + CH_3OH \longrightarrow NaI + NO + HSO_4CH_3$$

Chromates and dichromates react to a variable extent and no obvious stoichiometric relation has been deduced. Potassium permanganate is relatively unreactive, probably because of its insolubility. As mentioned earlier, some peroxides react with Karl Fischer reagent without interfering in the determination of water. The reaction probably involves the oxidation of sulfur dioxide rather than iodide.

Among the reducing agents, tin(II) chloride and sodium thiosulfate quantitatively reduce the iodine in Fischer reagent yielding a high value for the water content of the sample:

$$SnCl_2 \cdot 2H_2O + 3I_2 + 2SO_2 + 2CH_3OH \longrightarrow SnI_4 + 2HCl + 2HI + 2HSO_4CH_3$$

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[52] A. H. Laurene, *Anal. Chem.*, 24, 1496 (1952).

$$2Na_2S_2O_3\cdot 5H_2O + 11I_2 + 10SO_2 + 10CH_3OH \longrightarrow 2NaI + Na_2S_4O_6 + 20HI + 10HSO_4CH_3$$

Sodium sulfide is oxidized by Fischer reagent. The hydrate, $Na_2S\cdot 9H_2O$, showed values of 9.75 to 9.89 moles of apparent water per mole of hydrate instead of the expected 10 moles. Milberger *et al.*[41] observed that in the back-titration method hydrogen sulfide reacts mole for mole with iodine.

Hydroxylamine reduces the iodine in Karl Fischer reagent, but if sulfur dioxide and pyridine are added the hydroxylamine reacts preferentially with these latter compounds to form a sulfamate:

$$NH_2OH + SO_2 + C_5H_5N \longrightarrow C_5H_5N\cdot SO_3H\cdot NH_2$$

Since this reaction does not involve iodine, the interference of hydroxylamine in the determination of water can be eliminated by adding sulfur dioxide in pyridine to the sample before titrating.

Free ammonia interferes with the determination of water, possibly by nitrogen iodide formation, but the interference is readily eliminated by neutralizing the ammonia with acetic acid.

7. Determination of Water in Complex Materials. Of the methods available for the determination of water in complex materials, the Fischer method appears to be the most specific and widely applicable. Fischer reagent has been used successfully and conveniently for the determination of water in a variety of materials. The interference of simple compounds discussed in the preceding section must be considered and proper modifications and corrections made.

In some instances the water can be separated from the interfering components by extraction or distillation. Fischer[1] extracted water from dark-colored oils with methanol so visual titrations could be made. Other inert solvents such as ethylene glycol[53] may be used. Suter[50] separated water from interfering alkaline materials by azeotropic distillation with xylene and titrated water in the distillate with Fischer reagent (p. 433). Roberts and Levin[54] used benzene or pyridine for azeotropic distillation of water from oils and greases, whereas Rush and Kilbank[55] used the benzene-ethanol-water azeotrope to separate water from GR-S synthetic rubber. Homogeneous azeotropes such as ethanol-water should improve this method of separation by eliminating physical retention of water in the condenser. Rulfs[33] volatilized moisture from mineral samples and collected the water in a special condensing tube, then titrated it with Fischer reagent.

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[53] G. C. Gester, Jr., *Chem. Eng. Progr.*, **1**, No. 3, *Trans. Am. Inst. Chem. Engrs.*, **43**, 117 (1947); W. S. Hanna and A. B. Johnson, *Anal. Chem.*, **22**, 555 (1950).

[54] F. M. Roberts and H. Levin, *Anal. Chem.*, **21**, 1553 (1949).

[55] I. C. Rush and S. C. Kilbank, *Ind. Eng. Chem.*, **41**, 167 (1949).

With insoluble materials, it is usually necessary to reduce the sample to fine particles by grinding the solid or blending with solvent in a Waring Blendor so that extraction of water by an inert solvent is quantitative and reproducible. If the substance is slightly soluble in the solvent it may be possible to make a correction. For example, Gard and Butler[56] determined water in sodium bicarbonate by extracting with methanol. They titrated one aliquot with Fischer reagent to determine water plus dissolved sodium bicarbonate. A further aliquot was then titrated with standard hydrochloric acid to determine the dissolved sodium carbonate.

For most commercial materials no proven exact methods for the determination of water exist, so it is difficult to know the accuracy of the determination with Fischer reagent. However, the results obtained by the Fischer titration have been compared with those by other methods, such as oven-drying, desiccation or azeotropic distillation, as a means of estimating the accuracy of the method. The reproducibility of Fischer titrations has also been used as a measure of the accuracy. Most of the evidence available seems to indicate that the method does yield reliable values for water content in materials such as petroleum products, fats and oils, foods, carbohydrates and proteins, cellulose and wood products, resins, polymers and plastics, paints, and explosives. Generally only 15 minutes to 1 hour is required for the determination as compared with several hours for the other methods.

The Karl Fischer titration has been used extensively for the determination of moisture in petroleum products. The titration is made in a heterogeneous system in which the water is extracted by an immiscible solvent such as methanol or ethylene glycol,[53] or in a homogeneous system in which the petroleum products are made miscible with Fischer reagent by dissolving in a solvent such as a chloroform-methanol-pyridine mixture.[57] Aepli and McCarter[58] observed that gasolines containing tetraethyl lead cannot be analyzed by the Fischer method because of the reaction between tetraethyl lead and iodine.

Water in fats and oils has been determined by Fischer titration. Richter[59] obtained good checks for water in margarine and soybean oil by the Fischer and xylene distillation methods. Kaufmann and Funke[60] made more thorough investigations into the use of Fischer reagent for the determination of water in fats and oils. They extracted the moisture in methanol using decalin to prevent emulsification. The methanol phase was then titrated with Fischer reagent. If the oil does not contain interfering substances the two-phase system can be titrated directly without separation. A chloroform-methanol mixture (3:1) in which fats and oils are more soluble may be used.[61] The water determinations by the titration method agree well with those by xylene distillation, drying, and desiccation methods.

The Karl Fischer method has been applied to the determination of water in foodstuffs and the results obtained have been compared with those obtained

[56] L. N. Gard and R. C. Butler, *Anal. Chem.*, **26**, 1367 (1954).

[57] M. M. Acker and H. A. Frediani, *Ind. Eng. Chem., Anal. Ed.*, **17**, 793 (1945).

[58] O. T. Aepli and W. S. W. McCarter, *Ind. Eng. Chem., Anal. Ed.*, **17**, 316 (1945).

[59] Richter, *Angew. Chem.*, **48**, 776 (1935).

[60] H. P. Kaufmann and S. Funke, *Fette u. Seifen*, **44**, 345, 386 (1937).

[61] K. M. Brobst, *Anal. Chem.*, **20**, 939 (1948).

by electrical, drying, and distillation methods.[62] Solid materials are ground to pass through a 40 mesh sieve and the water is extracted by soaking or refluxing with methanol. The water is determined in the mixture by titrating directly with Fischer reagent or by adding an excess of reagent and back-titrating the excess with standard water-in-methanol solution. The back-titration method appears to yield more reproducible results than the direct-titration method, possibly because of more uniform extraction of water from the solids. On the other hand, if excess reagent is allowed to stand with the sample, high values are usually obtained because of side reactions, although McComb[62] observed that Fischer reagent in contact with protein materials for less than 1 hour does not undergo an appreciable amount of reaction. To make sure that sufficient time is allowed for complete extraction of water, the sample may be titrated after various periods or replicate samples may be allowed to stand with solvent for different intervals before titration, the apparent water content being plotted against the time. All indications are that the Karl Fischer titration does give accurate and specific water determinations. In dried foodstuffs the only compound reported which reacts with Fischer reagent is ascorbic acid. However, Johnson[62] has demonstrated that very few dried vegetables contain 10 mg. of ascorbic acid per gram, or the equivalent of 0.1 per cent apparent water. Most vegetables show less than 0.03 per cent apparent water from this reaction.

Water has been determined satisfactorily in sugars and sugar solutions,[63] native and processed cellulose materials,[64] explosives,[65] plastic molding powders,[66] paints and varnishes,[67] naval stores,[68] gases,[69] and liquid ammonia[70] using Karl Fischer reagent.

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[62] B. Makower, in *Analytical Methods in the Food Industry, Advances in Chem. Ser.*, No. 3, 37–54 (1950). R. H. Fosnot and R. W. Hamon, *Cereal Chem.*, **22**, 41 (1945); C. M. Johnson, *Ind. Eng. Chem., Anal. Ed.*, **17**, 312 (1945); B. Heinemann, *J. Dairy Sci.*, **28**, 845 (1945); C. W. Schroeder and J. H. Nair, *Anal. Chem.*, **20**, 452 (1948); E. A. McComb, *ibid.*, **20**, 1219 (1948).

[63] A. Zimmermann, *Fette u. Seifen*, **46**, 446 (1939); F. W. Zerban and L. Sattler, *Ind. Eng. Chem., Anal. Ed.*, **18**, 138 (1946); H. C. S. DeWhalley, *Intern. Sugar J.*, **53**, 157 (1951).

[64] J. Mitchell, Jr., *Ind. Eng. Chem., Anal. Ed.*, **12**, 390 (1940); C. D. McKinney, Jr., and R. T. Hall, *ibid.*, **15**, 460 (1943); R. P. Rennie and J. L. Monkman, *Can. Chem. Process Inds.*, **29**, 366 (1945).

[65] C. D. McKinney, Jr., and R. T. Hall, *Ind. Eng. Chem., Anal. Ed.*, **15**, 460 (1943); J. Hardy, W. D. Bonner, Jr., and R. M. Noyes, *ibid.*, **18**, 751 (1946); T. G. Bonner, *Analyst*, **71**, 483 (1946); R. P. Rennie and J. L. Monkman, *Can. Chem. Process Inds.*, **29**, 366 (1945); R. Dalbert and J. Tranchant, *Chimie & industrie*, **61**, 457 (1949).

[66] G. R. Cornish, *Plastics (London)*, **10**, 99 (1946).

[67] M. H. Swann, *Ind. Eng. Chem., Anal. Ed.*, **18**, 799 (1946); C. Whalley, *J. Oil & Colour Chemists' Assoc.*, **36**, 20 (1953).

These cover only a portion of the possible applications of the Fischer method but should serve to indicate its general applicability.[71] In any determination of water the possibility of using this method should be considered.

8. Other Applications of Fischer Reagent. The Karl Fischer reagent has been applied to the determination of a variety of organic functional groups. The groups to which these applications are made may be divided into two classes: (*a*) those which undergo reactions involving water; and (*b*) those which do not undergo reactions involving water but which themselves react stoichiometrically with Karl Fischer reagent.

ORGANIC FUNCTIONAL GROUPS UNDERGOING REACTIONS INVOLVING WATER

Alcoholic Hydroxyl Compounds: The basis of the Fischer titrimetric procedure for alcoholic hydroxyl groups is their esterification reaction with acetic acid:

$$\mathrm{ROH + CH_3COOH \xrightarrow{BF_3} CH_3COOR + H_2O}$$

By employing a large excess of acetic acid in the presence of boron trifluoride as an esterification catalyst, Bryant, Mitchell, and Smith[72] shifted the equilibrium almost completely to the right so that 1 mole of water is obtained per mole of alcoholic hydroxyl. The water thus formed is titrated directly with Karl Fischer reagent, after addition of pyridine to destroy the catalytic activity of the boron trifluoride.

Procedure: Weigh 5–10 ml. of alcohol sample (containing not more than 200 millimoles of hydroxyl) into a 100 ml. glass-stoppered volumetric flask which is about one third filled with dioxane. Dilute almost to the volume mark with dioxane, shake until homogeneous, and finally adjust to the volume mark. Transfer a 5 ml. aliquot portion of this solution to a 250 ml. glass-stoppered volumetric flask.[73] Add 20 ml. of catalyst solution,[74] stopper

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[68] V. E. Grotlisch and H. N. Burstein, *Ind. Eng. Chem., Anal. Ed.*, **17**, 382 (1945).

[69] A. G. Jones, *Analyst*, **76**, 5 (1951); W. Roman and A. Hirst, *ibid.*, 10.

[70] H. W. Hodgson and J. H. Glover, *ibid.*, **77**, 74 (1952).

[71] Cf. J. Mitchell, Jr., *Anal. Chem.*, **23**, 1069 (1951).

[72] W. M. D. Bryant, J. Mitchell, Jr., and D. M. Smith, *J. Am. Chem. Soc.*, **62**, 1 (1940).

[73] When convenient, a sample containing up to 10 meq. of hydroxyl may be weighed directly into the 250 ml. reaction flask. In this case the original sample is titrated directly for water and solvent is omitted from the blank.

[74] Dissolve about 100 g. of boron trifluoride and 1 or 2 ml. of water in sufficient glacial acetic acid to make 1 liter of solution.

the flask, and place, together with a blank containing 5 ml. of dioxane and 20 ml. of catalyst solution, in a water bath at 70°C. for 2 hours. The stoppers may be loosened momentarily to allow the expanded gases to escape. After 2 hours, remove the flasks from the water bath and allow to cool spontaneously to room temperature. Add 5 ml. of pyridine to each and titrate with Fischer reagent. After correction for the water in the dioxane, catalyst solution, pyridine, and the sample, the net water found is equivalent to the alcoholic hydroxyl in the sample. The water originally present is obtained by titrating 5 ml. of sample solution in dioxane and 5 ml. of pure dioxane separately, with Fischer reagent.

Calculations: Let the volumes of Karl Fischer reagent used in the above titrations be designated by the following:

A = ml. required for sample solution after esterification
B = ml. required for blank
C = ml. required for sample solution titrated directly
D = ml. required for pure dioxane

Further, let F represent the number of millimoles of water equivalent to 1 ml. of Fischer reagent and let V equal the volume of alcohol sample diluted to 100 ml. with dioxane:

$$\text{Millimoles of alcoholic hydroxyl in the sample} = (A - B - C + D)F$$

$$\text{Millimoles of water in the sample} = \left[C - D\left(\frac{100 - V}{1000}\right)\right]F$$

Notes: (1) The procedure is applicable to aliphatic and alicyclic alcohols including branched-chain types and hydroxy acids, also to aromatic alcohols having the hydroxyl group attached to an aliphatic side chain. Phenols react only partially and, by decreasing the catalyst concentration to 25 g. of boron trifluoride per liter, can be made to react negligibly whereas the aliphatic alcohols react completely. On the other hand, some unsaturated terpene alcohols give results higher than the theoretical.

(2) Tertiary alcohols may be dehydrated to olefins by the esterification treatment but, since this reaction yields 1 mole of water per mole of hydroxyl, these alcohols are determined quantitatively by this procedure.

(3) Aldehydes, ketones, acetals, and ketals interfere, probably by reactions similar to the following:

$$\mathrm{HCHO + 2CH_3COOH \longrightarrow (CH_3COO)_2CH_2 + H_2O}$$

$$\mathrm{CH_2(OCH_3)_2 + 4CH_3COOH \longrightarrow 2CH_3COOCH_3 + (CH_3COO)_2CH_2 + 2H_2O}$$

(4) Amines interfere by decreasing the activity of the catalyst.

(5) Normal esters in general do not interfere, but ortho esters react quantitatively with acetic acid to liberate water, probably by the reaction:[75]

$$\mathrm{RC(OR')_3 + 2CH_3COOH \longrightarrow RCOOR' + 2CH_3COOR' + H_2O}$$

(6) Mercaptans, like alcohols, are esterified by acetic acid in the presence of boron trifluoride:

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[75] D. M. Smith, J. Mitchell, Jr., and W. Hawkins, *J. Am. Chem. Soc.*, 66, 715 (1944).

$$RSH + CH_3COOH \longrightarrow CH_3COSR + H_2O$$

(7) Nitriles interfere by reacting with water in the presence of catalyst.
(8) The procedure is useful for determining both water and alcohol in mixtures. The accuracy of the procedure is about ±0.3 per cent.

Aliphatic Hydroxy Amines: By introducing certain changes in the esterification procedure for hydroxyl groups, Smith, Mitchell, and Hawkins[75] were able to determine amine alcohols in the presence of amines and ammonia. The procedure is basically the same as that for ordinary alcohols, but glacial acetic acid is substituted for dioxane as the reaction medium and the catalyst concentration is doubled.

Carboxylic Acids: By making use of the esterification of acids with methanol:

$$RCOOH + CH_3OH \xrightarrow{BF_3} RCOOCH_3 + H_2O$$

and titrating the liberated water with Karl Fischer reagent, Mitchell, Smith, and Bryant[76] worked out a procedure for the determination of carboxylic acids. Although simple acid-base titrations may be used to determine these substances, the Fischer titration procedure should be of value for the determination of carboxylic acids in the presence of weak inorganic acids having similar ionization constants.

Procedure: Weigh a 5–10 ml. sample, containing up to 160 meq. of carboxylic acid, into a 100 ml. glass-stoppered volumetric flask half-filled with dioxane. Dilute to the mark with dioxane, shaking the solution to assure homogeneity. Transfer a 5 ml. aliquot portion of this sample solution to a 250 ml. glass-stoppered volumetric flask,[77] add 20 ml. of catalyst solution,[78] stopper the flask, and place, along with a blank containing 5 ml. of dioxane and 20 ml. of catalyst solution, in a 60° water bath. The stoppers may be loosened momentarily to release pressure. After 1 hour, remove the flasks from the bath and allow to cool spontaneously to room temperature. Add 5 ml. of pyridine and titrate with Fischer reagent. After correction for water in the dioxane, catalyst solution, pyridine, and the sample, the net titer is equivalent to the carboxyl in the sample. Water in the sample is determined by titrating 5 ml. of sample solution and 5 ml. of pure dioxane separately with Fischer reagent and correcting for the dilution of dioxane by the sample in the sample solution (see p. 440).

Notes: (1) The procedure is applicable to aliphatic acids, including branched-chain and hydroxy-substituted types, and to aromatic acids having the carboxyl group attached to an aliphatic side chain. Aromatic acids having the carboxyl group attached to the aromatic ring do not react quantitatively. By reducing the catalyst concentration the aliphatic acids can be determined in the presence of the aromatic acids.

[76] J. Mitchell, Jr., D. M. Smith, and W. M. D. Bryant, *J. Am. Chem. Soc.*, 62, 4 (1940).

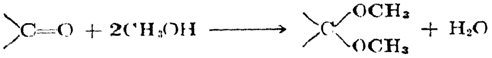
[77] A portion of sample containing up to 8 meq. of carboxylic acid may be weighed directly into the reaction flask, avoiding the use of dioxane in the sample and blank. This must be done with solid acid samples having a limited solubility in dioxane.

[78] Dissolve about 100 g. of boron trifluoride and 2 ml. of water in sufficient methanol to make 1 liter of solution.

(2) The precision and accuracy of the procedure are about ±0.3 per cent by comparison with alkali titrations.

(3) Esters, acetals, amides, nitriles, unsaturated alcohols, and unsaturated hydrocarbons do not react. Amines and amino acids may inhibit the activity of the catalyst.

(4) Carbonyl compounds interfere by reacting with methanol:



$$>C{=}O + 2CH_3OH \longrightarrow >C(OCH_3)_2 + H_2O$$

The reaction is quantitative, so appropriate corrections may be made. The use of hydrogen cyanide to eliminate the carbonyl interference (p. 428) fails since carboxylic acids are only partially esterified under these conditions.

(5) Readily dehydrated substances such as tertiary alcohols interfere.

(6) Sulfuric and boric acids are the only inorganic acids known to interfere because of ester formation:

$$H_2SO_4 + CH_3OH \longrightarrow CH_3HSO_4 + H_2O$$

$$H_3BO_3 + 3CH_3OH \longrightarrow B(OCH_3)_3 + 3H_2O$$

(7) Acid anhydrides interfere probably by ester formation:

$$(RCO)_2O + 2CH_3OH \longrightarrow 2RCOOCH_3 + H_2O$$

Acid Anhydrides: Smith, Bryant, and Mitchell[79] developed two procedures for the determination of acid anhydrides using Karl Fischer reagent. Both are based on hydrolysis of the anhydrides with a slight excess of water:

$$(RCO)_2O + H_2O \longrightarrow 2RCOOH$$

In one procedure the hydrolysis is carried out in acetic acid solution with boron trifluoride as catalyst, whereas in the other, more widely applicable method the hydrolysis is carried out in pyridine solution with sodium iodide as catalyst.

Acid Hydrolysis Procedure: Weigh a sample containing up to 4 millimoles of anhydride into a 250 ml. glass-stoppered volumetric flask.[80] Add 20 ml. of catalyst solution,[81] stopper the flask, and place in a 60° water bath, along with a blank containing 20 ml. of catalyst solution (and 5 ml. of glacial acetic acid if an aliquot portion of the sample in acetic acid is used). Loosen the stoppers momentarily to release the pressure of expanded gases, stopper tightly, and heat for 2 hours. Remove the flasks from the bath and allow to cool to room temperature. Carefully add 5 ml. of pyridine to each flask and titrate the excess water with Fischer reagent. The difference between these two titers is equivalent to the total anhydride content of the sample.[82]

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[79] D. M. Smith, W. M. D. Bryant, and J. Mitchell, Jr., *J. Am. Chem. Soc.*, 62, 608 (1940); 63, 1700 (1941).

[80] The sample may be prepared as an acetic acid solution such that a 5 ml. aliquot portion may be used in the procedure.

[81] Dissolve about 100 g. of boron trifluoride and 4 ml. of water in glacial acetic acid to make 1 liter of solution.

Notes: (1) The procedure is applicable to acyclic, aliphatic anhydrides. The precision and accuracy are within ±0.3 per cent based on comparison with values obtained by the sodium hydroxide-sodium methylate method. Glutaric anhydride is hydrolyzed quantitatively, but other dibasic acid anhydrides react incompletely. Benzoic anhydride reacts completely.

(2) The procedure is affected adversely by the same compounds which interfere with the determination of alcohols.

Alkaline Hydrolysis Procedure: Weigh a sample containing 8 to 10 millimoles of anhydride into a 250 ml. glass-stoppered volumetric flask.[83] Add 25 ml. of catalyst solution.[84] Place the flask, together with a blank containing 25 ml. of catalyst solution (and 5 ml. of pyridine if a pyridine solution of the sample is used), in a 60° water bath. Loosen the stoppers momentarily and keep the flasks hot for 1 hour. Remove the flasks from the bath, allow to cool to room temperature, and titrate the excess water in each with Fischer reagent. The difference between the two titers is equivalent to the total anhydride plus water in the sample. The water content of anhydrides is usually very small but may be determined readily by titrating a portion of the sample with Karl Fischer reagent at 0°C. At this temperature anhydrides react very slowly with water but Fischer reagent reacts quickly.

Notes: (1) The precision and accuracy of the procedure are within ±0.3 per cent based on comparison with values obtained by the sodium hydroxide-sodium methylate method.

(2) Dibasic acid anhydrides react quantitatively, whereas by the acid hydrolysis method only glutaric anhydride gave quantitative results. Maleic anhydride reacts violently with pyridine reagent and could not be analyzed. Camphoric acid, probably because of steric hindrance, reacted to the extent of only 1 per cent.

Acid Chlorides: Seaman *et al.*[85] reported a method for determining acetylsulfanilyl chloride with Karl Fischer reagent, based on hydrolysis:

$$CH_3CO—NH—C_6H_4—SO_2Cl + H_2O \longrightarrow CH_3CO—NH—C_6H_4—SO_3H + HCl$$

In the presence of pyridine the reaction takes place quickly, but in its absence the reaction is very slow and proceeds only to a slight extent. The method was developed for the compound mentioned but is applicable to other acid chlorides.

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[82] If the aliquot portion of sample in acetic acid solution is used, proper corrections for dilution of the solvent by the sample must be applied. Acid anhydrides generally do not contain water but, if desired, water in the sample can be titrated directly with Fischer reagent in the absence of catalyst solution.

[83] If more convenient, a 5 ml. aliquot of a pyridine solution of the sample may be used instead of the weighed sample.

[84] Dissolve 100 g. of sodium iodide and 8 ml. of water in pyridine to make 1 liter of solution.

[85] W. Seaman, A. R. Norton, J. T. Woods, and E. A. Massad, *Ind. Eng. Chem., Anal. Ed.*, 16, 517 (1944).

Carbonyl Compounds: The liberation of water by the reaction of carbonyl compounds with hydroxylamine hydrochloride is used as the basis for a determination of carbonyl compounds by titration with Karl Fischer reagent:[86]

$$>C{=}O + H_2NOH\cdot HCl \longrightarrow >C{=}NOH + HCl + H_2O$$

The oximes formed are unreactive toward Fischer reagent, but hydroxylamine reacts in some unknown manner to yield water. Consequently, the excess hydroxylamine salt remaining after the formation of oxime must be stabilized before titration of water. This is done by adding an excess of sulfur dioxide and pyridine in methanol to the reaction mixture 10 minutes before titration. The reaction involved is probably:

$$H_2NOH\cdot HCl + SO_2 + 2C_5H_5N \longrightarrow C_5H_5N\cdot HSO_3NH_2 + C_5H_5N\cdot HCl$$

Procedure: Into a 100 ml. glass-stoppered volumetric flask weigh a 5–10 ml. sample containing not more than 0.1 mole of carbonyl or water. Dilute to the volume mark with methanol. Transfer a 10 ml. aliquot portion of this solution to a 250 ml. glass-stoppered volumetric flask containing 30 ml. of 0.5*N* hydroxylamine hydrochloride solution in methanol[87] and 5 ml. of pyridine. Place the flask in a 60° water bath, loosen the stopper momentarily to release pressure, tighten, and heat for 2 hours. Remove the flask from the bath and allow to cool to room temperature. Add 25 ml. of sulfur dioxide reagent,[88] allow to stand for 10 minutes to an hour, and titrate the solution with Fischer reagent. Run a blank titration with the reagents and determine the water content of the sample by titration with Fischer reagent after treatment with hydrocyanic acid (see p. 428).

The titer for the sample less that for the blank is calculated to millimoles of water. The net result after deduction of the water initially present in the sample is equivalent, mole for mole, to the carbonyl content.

Notes: (1) The method is applicable to aliphatic, alicyclic and aromatic aldehydes and ketones. Camphor is the only compound studied that reacts incompletely. The average precision and accuracy of the method are about ±0.3 per cent.

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[86] J. Mitchell, Jr., D. M. Smith, and W. M. D. Bryant, *J. Am. Chem. Soc.*, **63**, 573 (1941).

[87] Dissolve 35 g. of hydroxylamine hydrochloride in sufficient methanol to make 1 liter of solution.

[88] Add 45 ml. of liquid sulfur dioxide to a chilled solution of 80 ml. of pyridine and 875 ml. of methanol.

(2) High concentrations of acids, ethers, esters, and hydrocarbons show no interference with the method. If esterification catalysts are present, organic acids react with methanol; therefore samples containing acids are diluted with pyridine rather than methanol.

Amines: Acetic anhydride in pyridine acetylates primary and secondary amines according to the reactions:

$$\begin{aligned} RNH_2 + (CH_3CO)_2O &\longrightarrow CH_3CONHR + CH_3COOH \\ RNHR' + (CH_3CO)_2O &\longrightarrow CH_3CONRR' + CH_3COOH \end{aligned}$$

By hydrolyzing the excess acetic anhydride after these reactions and titrating the excess water with Karl Fischer reagent, Mitchell, Hawkins, and Smith[89] were able to determine the sum of the primary and secondary amines in a mixture. For the determination of primary amines only, a Schiff reaction is carried out with benzaldehyde:[90]

$$RNH_2 + C_6H_5CHO \longrightarrow RN{=}CHC_6H_5 + H_2O$$

The water produced is determined by the Fischer method after deactivation of excess aldehyde with a solution of hydrogen cyanide in pyridine.

Acetylation of the primary plus secondary amines takes place in 30 minutes at room temperature, in the presence of pyridine. Hydrolysis of the excess anhydride, catalyzed by sodium iodide, requires an equal period at 60°C. Diaryl secondary amines and pyrrole fail to react with acetic anhydride. The benzaldehyde reaction for primary amines is carried out in 15–30 minutes at 60°, deactivation with cyanide requiring 45 minutes at room temperature. For full details of the procedures, and for data on interfering substances, the original papers should be consulted.

Nitriles: A method based on the quantitative hydrolysis of nitriles in the presence of boron trifluoride-acetic acid catalyst was developed by Mitchell and Hawkins:[91]

$$RCN + H_2O \longrightarrow RCONH_2$$

The excess water is titrated directly with Karl Fischer reagent.

Procedure: Weigh a portion of sample containing up to 10 millimoles of nitrile into a 250 ml. glass-stoppered volumetric flask. Add 20 ml. of hydrolysis reagent,[92] stopper the flask, and place in an 80° water bath for 2 hours. Remove the flask from the bath and allow to cool to room temperature. Place in an ice bath and carefully add 15 ml. of pyridine. Titrate the solution with Fischer reagent. Run a blank on the reagents and determine the water content of the sample by direct titration with Fischer reagent.

The net titer corrected for the water content of the sample is equivalent to the nitrile present.

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[89] J. Mitchell, Jr., W. Hawkins, and D. M. Smith, *J. Am. Chem. Soc.*, 66, 782 (1944).

[90] W. Hawkins, D. M. Smith, and J. Mitchell, Jr., *J. Am. Chem. Soc.*, 66, 1662 (1944); cf. p. 346 of ref. 2.

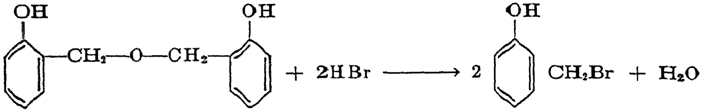
[91] J. Mitchell, Jr., and W. Hawkins, *J. Am. Chem. Soc.*, 67, 777 (1945).

[92] Dissolve 300 g. of boron trifluoride and 6.5 ml. of water in 500 ml. of acetic acid.

Notes: (1) The method is applicable to normal lower aliphatic and several aromatic nitriles, and to nitriles of dibasic acids. Aromatic nitriles differ in their behavior. Although *m*- and *p*-toluonitrile react quantitatively, *o*-toluonitrile and α-naphthonitrile react incompletely. Methyleneaminoacetonitrile, cyanoacetonitrile, and cyanoacetic acid also react incompletely.

(2) Alcohols and those substances which interfere with the Karl Fischer alcohol hydroxyl method interfere also with the nitrile method. Little or no interference is observed with amides.

Other Compounds: Lilley and Osmond[93] developed a method for the determination of ether linkages in phenol alcohols and derived resins, based on the Fischer titration of water formed by the reaction:



Methylol groups present in the sample also react slowly with hydrogen bromide to yield water:

$$RCH_2OH + HBr \longrightarrow RCH_2Br + H_2O$$

These groups are determined independently by an iodometric method[94] and appropriate corrections are made.

The Karl Fischer reagent also has been applied to the determination of hydroperoxides and dialkyl peroxides.[95] These are reduced to alcohols by powdered zinc and acetic acid:

$$ROOH + 2[H] \longrightarrow ROH + H_2O$$

$$ROOR + 2[H] \longrightarrow 2ROH$$

The alcohols are esterified and titrated with Fischer reagent essentially as in the alcohol procedure. Diacyl peroxides, such as benzoyl peroxide, do not interfere.

FUNCTIONAL GROUP REACTIONS INVOLVING NO WATER[96]

Mercaptans: Mercaptans are oxidized to disulfides by the iodine in Karl Fischer reagent. Their interference in the determination of water can be avoided by addition of active olefins (see p. 429). The difference in titer between the direct and the modified titrations is equivalent to the mercaptan present in the sample. Since other methods are available for the determination of mercaptans, this procedure is not of great importance.

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[93] H. S. Lilley and D. W. J. Osmond, *J. Soc. Chem. Ind.* (*London*), 66, 425 (1947).

[94] H. S. Lilley and D. W. J. Osmond, *J. Soc. Chem. Ind.* (*London*), 66, 340 (1947).

[95] Ref. 2, p. 361–367.

[96] Ref. 2, pp. 375 ff.

Metal Salts of Organic Acids: In the presence of boron trifluoride as catalyst, metal salts of organic acids are esterified by methanol yielding alkali which is titratable with Karl Fischer reagent:

$$\mathrm{RCOOM + CH_3OH \xrightarrow{BF_3} RCOOCH_3 + MOH}$$
$$\mathrm{MOH + I_2 + SO_2 + CH_3OH \longrightarrow MI + HI + HSO_4CH_3}$$

As is observed in the Karl Fischer carboxyl procedure, the salts of aromatic acids do not react quantitatively. Since acidimetric titrations can be used to determine these salts, this procedure is not of great importance.

Esters: Esters are saponified by alkali metal hydroxides:

$$\mathrm{RCOOR' + MOH \longrightarrow RCOOM + R'OH}$$

Since the hydroxides are titrated the same as water with Karl Fischer reagent, the saponification reaction can be used to determine esters through the amount of alkali used. Acids present in esters also react with the alkali but, since a mole of water is produced per mole of alkali used, this introduces no interference.

$$\mathrm{RCOOH + MOH \longrightarrow RCOOM + H_2O}$$

Procedure: Weigh a portion of sample containing up to 5 meq. of ester plus acid into a 250 ml. glass-stoppered volumetric flask with a grooved stopper. (A groove cut around the stopper and filled with a high melting point stopcock grease makes an effective seal at elevated temperatures.) Add 10 ml. of saponification reagent[97] and fasten the greased stopper with a spring clamp. Prepare a blank with 10 ml. of reagent. Place both flasks in a 130° oven for 30 minutes, remove, allow to cool to room temperature, and titrate the solution in each with Fischer reagent. The net millimoles of apparent water found, corrected for the water content of the sample, is equivalent to the ester content of the sample.

INORGANIC SUBSTANCES

Sulfur Trioxide in Fuming Sulfuric Acid:[98] The procedure is based on the reaction of sulfur trioxide with an excess of water, to form sulfuric acid, and titration of the unused water with Karl Fischer reagent.

Procedure: Pipette an exactly reproducible volume (about 2 ml.) of concentrated sulfuric acid into a 250 ml. glass-stoppered volumetric flask. Weigh in 2–2.5 g. of sample, making sure that the sample drops directly into the acid. Cool the flask in an ice bath and carefully add 30 ml. of a cold 1:1 mixture of pyridine and dioxane. Allow to cool to room temperature and titrate with Fischer reagent. Titrate a blank containing 2 ml. of sulfuric acid and 30 ml. of pyridine-dioxane reagent. The net titer is equivalent to the sulfur trioxide content of the sample.

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[97] Use 1N potassium hydroxide in technical grade diethylene glycol. Weigh 14.5 g. of potassium hydroxide pellets into a 250 ml. glass-stoppered volumetric flask and dissolve in 100 ml. of glycol at 60°. Cool to room temperature and dilute to volume with more glycol.

[98] Ref. 2, p. 385–387.

Note: This procedure should be applicable to the determination of sulfur trioxide in other materials such as sulfur dioxide.

Silanols.[99] Most silanols and silanediols can be titrated with Karl Fischer reagent according to the reaction:

$$R_3SiOH + I_2 + SO_2 + 2CH_3OH \longrightarrow R_3SiOCH_3 + 2HI + HSO_4CH_3$$

Procedure: Titrate 5 ml. of pyridine or methanol in a dry 50 ml. glass-stoppered volumetric flask with Fischer reagent. Add the weighed sample, shake, and again titrate. The volume of reagent used in the second titration corresponds to the silanol content of the sample.

Notes: (1) The reaction involved is analogous to that for orthoboric acid and is also shown by hydroxy compounds of other heavy elements of Group IVB, such as triphenyl tin hydroxide and triphenyl lead hydroxide.

(2) The procedure yields good results with silanols; however, tri-1-naphthylsilanol and tri-*o*-tolylsilanol do not react appreciably owing to steric hindrance. Hexamethyldisiloxane, hexaphenyldisiloxane, ethyl triethoxysilane, tris(*p*-chlorophenyl)ethoxysilane, triphenylchlorosilane, and tris(*p*-dimethylaminophenyl)silane could not be titrated accurately.

[99] H. Gilman and L. S. Miller, *J. Am. Chem. Soc.*, **73**, 2367 (1951).

CHAPTER X

POTASSIUM IODATE AS OXIDIZING TITRANT

1. General Considerations. When potassium iodate is used as an oxidant, the course of the reaction is influenced markedly by the medium and by the nature of the reactants. The reaction in a weakly acid medium has already been considered (p. 235), free iodine being the end-product. The main applications of this reaction are in the standardization of thiosulfate and in the determination of acidity (p. 276). When very powerful reducing agents are present, however (e.g., Ti^{3+}), the reaction proceeds further and free iodine is reduced to iodide.

In a medium strongly acid to hydrochloric acid, the reaction follows an entirely different course, iodine being oxidized to iodine monochloride:

$$I_2 + 2Cl^- \longrightarrow 2ICl + 2e$$

This is the most important of the reactions of potassium iodate, and it is under such conditions of acidity that the reagent is used extensively as a titrant.

The equilibria which are involved have been studied by several investigators,[1] the general conclusion being that, in the presence of an excess of hydrochloric acid, iodine monochloride forms a complex ion:

$$ICl + Cl^- \rightleftharpoons ICl_2^-$$

Philbrick, however, claimed that he could find no evidence for the formation of complex ions and he considered that complete dissociation of iodine mono-

$$ICl \longrightarrow I^+ + Cl^-$$

chloride occurred which would explain the reason for the carbon tetrachloride remaining colorless when shaken with the solution, whereas pure iodine monochloride would be expected to dissolve in and color the solvent.

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[1] G. S. Forbes, S. W. Glass, and R. M. Fuoss, *J. Am. Chem. Soc.*, **47**, 2892 (1925); E. H. Swift, *ibid.*, **52**, 894 (1930); J. H. Faull and S. Baeckström, *ibid.*, **54**, 620 (1932); F. A. Philbrick, *J. Chem. Soc.*, **1930**, 2254.

Philbrick's findings were adversely criticized by Faull and Baeckstrȫm, who maintained that the iodine cation was present in negligible concentrations as was shown from specific conductivity and transference experiments. In a later paper, Philbrick[2] described a further series of experiments in which he studied the hydrolysis of iodine monochloride and from which he concluded that the complex ion ICl_2^- is indeed present. The dissociation of iodine monochloride takes place only partly even at great dilutions; in an excess of hydrochloric acid, the dissociation is negligible. He considered that some other explanation must account for the solvent action of these solutions on free iodine which had previously misled him to believe that the iodine cation was formed in large quantities.

According to Lang,[3] when the concentration of hydrochloric acid is low, a significant amount of I^+ is produced and hydrolyzes as follows:

$$I^+ + H_2O \rightleftharpoons HOI + H^+$$

If this reaction occurs to any great extent, an overconsumption of iodate will take place owing to the formation of free iodine from hypoiodous acid.

$$5HOI \rightleftharpoons 2I_2 + IO_3^- + H^+ + 2H_2O$$

The hydrolysis is readily avoided by ensuring that the concentration of hydrochloric acid is never less than 3.5–4*N* (or 12 per cent actual hydrochloric acid) at the end-point.

Swift,[4] however, suggests that it is the rate of reaction near the end-point which is affected by low acidity, rather than the hydrolysis of iodine monochloride, because iodine monochloride can be largely diluted without much iodine being formed and because certain titrations can be made satisfactorily at an acidity of 2*N* or even lower (pp. 457 and 461). Philbrick's later experiments[2] support this view.

Oxidation by iodate in a large excess of hydrochloric acid proceeds through several stages:

$$IO_3^- + 6H^+ + 6e \longrightarrow I^- + 3H_2O \quad (1)$$

$$IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O \quad (2)$$

$$IO_3^- + 2I_2 + 6H^+ \longrightarrow 5I^+ + 3H_2O \quad (3)$$

Accordingly, in the initial stages of the titration, free iodine is liberated, but, as more titrant is added, this is oxidized to iodine monochloride and the dark color of the solution gradually lightens. The above reactions may be summarized as follows:

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[2] F. A. Philbrick, *J. Am. Chem. Soc.*, **56**, 1257 (1934).

[3] R. Lang, *Z. anal. Chem.*, **106**, 12 (1936).

[4] E. H. Swift, *J. Am. Chem. Soc.*, **52**, 894 (1930).

$$IO_3^- + 6H^+ + 4e \longrightarrow I^+ + 3H_2O \qquad (4)$$

Hence, under these conditions, the equivalent weight is one fourth the molecular weight, i.e., 53.504.

Detection of the End-Point. *Immiscible Solvent:* To detect the end-point, an immiscible solvent which gives an intense violet color with free iodine, such as carbon tetrachloride or chloroform, is added to the test solution. The latter is contained in a glass-stoppered bottle or Erlenmeyer flask and is shaken well after each addition of titrant. The end-point is marked by the disappearance of the last trace of violet color from the solvent, and is extremely sharp. Iodine monochloride is not extracted and only imparts a faint yellowish color to the aqueous phase.

The method was first used by Andrews[5] and appears to have been based on earlier work by Dupré and Dupré[6] (who used chlorine water as the oxidant and appear to be the first to have used immiscible solvents to mark the end-point), and McCulloch,[7] who oxidized with potassium permanganate. The methods of Andrews were later extended by Jamieson,[8] who developed further direct and indirect methods.

Other oxidants have been used in place of iodate, iodine monochloride first being added as indicator. Swift[4] used potassium permanganate, ceric sulfate, and potassium dichromate. The acid concentration at the end-point with the first two reagents should not be less than $4N$; and with potassium dichromate not less than $8N$. Chloramine T,[9] chloramine B,[10] potassium periodate,[11] and sodium vanadate[12] have also been used.

[5] L. W. Andrews, *J. Am. Chem. Soc.*, **25**, 756 (1903); *Z. anorg. Chem.*, **36**, 76 (1903).

[6] A. Dupré and F. Dupré, *Ann.*, **94**, 365 (1855).

[7] N. McCulloch, *Chem. News*, **57**, 45, 135 (1888); *ibid.*, **60**, 259 (1889); *Z. anal. Chem.*, **31**, 700 (1892).

[8] G. S. Jamieson, *Volumetric Iodate Methods*, Chemical Catalog Co., New York, 1926.

[9] A. J. Berry, *Analyst*, **59**, 736 (1934).

[10] B. Singh and K. C. Sood, *Anal. Chim. Acta*, **11**, 313, 317 (1954).

[11] B. Singh and A. Singh, *J. Indian Chem. Soc.*, **29**, 34 (1952).

[12] B. Singh and R. Singh, *Anal. Chim. Acta*, **10**, 408 (1954); **11**, 412 (1954); **13**, 405 (1955).

Dyestuffs as Indicators: Smith and Wilcox[13] examined the possibility of using certain dyestuffs as irreversible indicators, in place of an immiscible solvent, to avoid the tedium of stoppering and shaking the vessel between each addition of the titrant.

Several dyestuffs were examined. Amaranth (*C.I.* 184) was destroyed between acidities of 3–5*M* at 30°C. or above and changed from red to colorless. Brilliant ponceau 5R (*C.I.* 185) changed from orange to colorless at acidities greater than 3*M* at 25–30°C. and between 4 and 5*M* at higher temperatures. Naphthol blue black (*C.I.* 246) also changed, but more slowly and appears to be less satisfactory. The remaining dyestuffs which were examined were unsuitable.

It is necessary to delay the addition of the indicator until the endpoint is approached, otherwise it will be destroyed prematurely.

Indicator Blanks: One milliliter of a 0.2 per cent aqueous solution of indicator is destroyed by 0.05 ml. of 0.1*N* iodate solution. Accordingly, the blank is negligible, for less than 0.5 ml. is required for each titration. It would be desirable, nevertheless, to check the blank on each new batch of indicator owing to the variable composition of such dyestuffs.

The most suitable indicators for a particular titration are shown in Table I.

TABLE I

Determination	Indicator recommended
As^{3+}	Amaranth,[a] brilliant ponceau 5R[b]
Sb^{3+}	Amaranth[a]
Fe^{2+}	Amaranth, brilliant ponceau 5R, naphthol blue black[c]
Tl^{+}	Amaranth
$S_2O_3^{2-}$	Amaranth
CNS^{-}	Amaranth, brilliant ponceau 5R, naphthol blue black
SO_3^{2-}	Amaranth
N_2H_4	Amaranth, brilliant ponceau 5R
$N_2H_3C_6H_5$	Brilliant ponceau 5R

[a] *C.I.* 184. [b] *C.I.* 185. [c] *C.I.* 246.

Belcher and Clark[14] found that *p*-ethoxychrysoidine can also be used as indicator and has reversible properties. Many commercial preparations are impure, however, and although a sharp end-point is still obtained the color change may not be reversible. The blank value of each new batch must be determined, for these can vary appreciably. Just before the end-point the pink color changes to red-purple. This changes to orange at the end-point. When a few drops of standard arsenite solution are added, the color reverts to a faint pink which deepens as more iodate is cautiously added; the reduction of the indicator is induced by the arsenite-iodate reaction. There is a certain amount of destruction, for the reversal cannot be done more than twice.

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[13] G. F. Smith and C. S. Wilcox, *Ind. Eng. Chem., Anal. Ed.*, 14, 49 (1942).

[14] R. Belcher and S. J. Clark, *Anal. Chim. Acta*, 4, 580 (1950).

The following equations illustrate some of the more important reactions in which potassium iodate is used as titrant:

$$2\mathrm{KI} + \mathrm{KIO_3} + 6\mathrm{HCl} \longrightarrow 3\mathrm{KCl} + 3\mathrm{ICl} + 3\mathrm{H_2O}$$

$$2\mathrm{I_2} + \mathrm{KIO_3} + 6\mathrm{HCl} \longrightarrow \mathrm{KCl} + 5\mathrm{ICl} + 3\mathrm{H_2O}$$

$$\mathrm{As_2O_3} + \mathrm{KIO_3} + 2\mathrm{HCl} \longrightarrow \mathrm{As_2O_5} + \mathrm{ICl} + \mathrm{KCl} + \mathrm{H_2O}$$

$$\mathrm{Sb_2O_3} + \mathrm{KIO_3} + 2\mathrm{HCl} \longrightarrow \mathrm{Sb_2O_5} + \mathrm{ICl} + \mathrm{KCl} + \mathrm{H_2O}$$

$$2\mathrm{SnCl_2} + \mathrm{KIO_3} + 6\mathrm{HCl} \longrightarrow 2\mathrm{SnCl_4} + \mathrm{KCl} + \mathrm{ICl} + 3\mathrm{H_2O}$$

$$2\mathrm{Hg_2Cl_2} + \mathrm{KIO_3} + 6\mathrm{HCl} \longrightarrow 4\mathrm{HgCl_2} + \mathrm{KCl} + \mathrm{ICl} + 3\mathrm{H_2O}$$

$$2\mathrm{TlCl} + \mathrm{KIO_3} + 6\mathrm{HCl} \longrightarrow 2\mathrm{TlCl_3} + \mathrm{KCl} + \mathrm{ICl} + 3\mathrm{H_2O}$$

$$\mathrm{N_2H_4} + \mathrm{KIO_3} + 2\mathrm{HCl} \longrightarrow \mathrm{KCl} + \mathrm{ICl} + \mathrm{N_2} + 3\mathrm{H_2O}$$

$$\mathrm{C_6H_5NH.NH_2} + \mathrm{KIO_3} + 2\mathrm{HCl} \longrightarrow \mathrm{KCl} + \mathrm{ICl} + \mathrm{N_2} + \mathrm{C_6H_5OH} + 2\mathrm{H_2O}$$

$$2\mathrm{SO_2} + \mathrm{KIO_3} + 2\mathrm{HCl} + \mathrm{H_2O} \longrightarrow 2\mathrm{H_2SO_4} + \mathrm{ICl} + \mathrm{KCl}$$

$$\mathrm{Na_2S_2O_3} + 2\mathrm{KIO_3} + 2\mathrm{HCl} \longrightarrow \mathrm{Na_2SO_4} + \mathrm{K_2SO_4} + 2\mathrm{ICl} + \mathrm{H_2O}$$

$$2\mathrm{Na_2S_4O_6} + 7\mathrm{KIO_3} + 10\mathrm{HCl} \longrightarrow 4\mathrm{H_2SO_4} + 2\mathrm{Na_2SO_4} + 2\mathrm{K_2SO_4} + 3\mathrm{KCl} + 7\mathrm{ICl} + \mathrm{H_2O}$$

$$2\mathrm{KCNS} + 3\mathrm{KIO_3} + 2\mathrm{HCl} \longrightarrow 2\mathrm{K_2SO_4} + 2\mathrm{ICN} + \mathrm{ICl} + \mathrm{KCl} + \mathrm{H_2O}$$

When small amounts of material are being determined, and in certain titrations, iodine may be oxidized in preference to the reducing agent present, in which event a false end-point is obtained and the iodine color reappears repeatedly. In such cases, it is necessary to pretreat with iodine monochloride. An equivalent amount of iodine is released:

$$2\mathrm{I}^+ + 2e \longrightarrow \mathrm{I_2}$$

The titer obtained is independent of the amount of iodine monochloride which has been added.

Ferrous iron may be determined in this way:[15]

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[15] G. B. Heisig, *J. Am. Chem. Soc.*, 50, 1687 (1928).

$$2Fe^{2+} + 2ICl \longrightarrow I_2 + 2Fe^{3+} + 2Cl^-$$
$$2I_2 + KIO_3 + 6HCl \longrightarrow KCl + 5ICl + 3H_2O$$

The titration may be done in the presence of many organic substances.

In addition, many indirect determinations are possible. For example, substances which oxidize arsenious oxide (e.g., hydrogen peroxide) or potassium iodide (e.g., peroxides) may be determined by adding a known excess of a standard solution of the appropriate reagent and then back-titrating with potassium iodate solution.

Copper,[16] zinc,[17] and mercury[18] may be determined by precipitating as simple or double thiocyanates and titrating the thiocyanate in the washed precipitate:

$$2Cu_2(CNS)_2 + 7KIO_3 + 14HCl \longrightarrow 7KCl + 4CuSO_4 + 7ICl + 4HCN + 5H_2O$$
$$HgZn(CNS)_4 + 6KIO_3 + 12HCl \longrightarrow HgSO_4 + ZnSO_4 + 2H_2SO_4 + 6ICl + 4HCN + 6KCl + 2H_2O$$

Lead[19] and mercury[20] may be determined by precipitating as the paraperiodates, dissolving the precipitates in an excess of standard arsenious oxide solution and hydrochloric acid and back-titrating with potassium iodate solution.

The Iodine-Cyanide Method: Lang[21] has developed methods (p. 469) in which the iodine cation is stabilized by the formation of iodine cyanide.

$$I^+ + HCN \rightleftharpoons ICN + H^+$$

In the presence of hydrocyanic acid, oxidation proceeds rapidly at concentrations not less than $1N$ in hydrochloric or $2N$ in sulfuric acid, provided that some chloride is present. In the absence of chloride the oxidation proceeds more slowly. Starch may be used as indicator because of the more favorable conditions of acidity.

The equilibrium is represented by the following equation:

$$I_2 + HCN \rightleftharpoons ICN + I^- + H^+$$

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[16] G. S. Jamieson, L. H. Levy, and H. L. Wells, *J. Am. Chem. Soc.*, **30**, 760 (1908).

[17] G. S. Jamieson, *ibid.*, **40**, 1036 (1918).

[18] *Idem, Ind. Eng. Chem.*, **11**, 296 (1919).

[19] H. H. Willard and J. J. Thompson, *Ind. Eng. Chem., Anal. Ed.*, **6**, 425 (1934).

[20] *Idem, ibid.*, **3**, 398 (1931).

[21] R. Lang, *Z. anorg. Chem.*, **122**, 332 (1922); **142**, 229, 280 (1925); **144**, 75 (1925).

There is no risk of hydrolysis, for under these conditions iodine cyanide does not dissociate significantly; at room temperature it decomposes only in alkaline solution.

Iodine monochloride is formed intermediately and is converted to iodine cyanide, the speed of the conversion depending on the concentration of hydrochloric and hydrocyanic acids. If the starch-iodine reaction occurs too slowly as the end-point is approached, the solution must be diluted with water or partially neutralized with ammonia solution or more hydrocyanic acid should be added.

The method may be used in the presence of an excess of bromide. If the titrant is added rapidly, the permissible amount present must not exceed 1 g. of potassium bromide per 100 ml. A greater concentration may be tolerated when the titrant is added slowly. The bromide concentration must be lower when a sulfuric acid medium is used.

As the end-point is approached bromides cause a color change after each drop from red-brown through violet to blue. Each further addition must then be delayed until the violet color is formed, otherwise a sharp end-point cannot be obtained.

As in the Andrews method, other oxidants may be used[22] in place of iodate after the addition of iodine monochloride or iodine-cyanide, e.g., periodate, permanganate, ceric sulfate, chloramine T, and bromate.

The Iodo-acetone Method: In this method due to Berg,[23] the iodate titration is done in the presence of acetone (cf. p. 473):

$$I^+ + C_3H_6O \longrightarrow C_3H_5OI + H^+$$

The equilibrium is analogous to that in the Lang procedure:

$$I_2 + C_3H_6O \rightleftharpoons C_3H_5OI + I^-$$

The titration is carried out in 2–2.5N sulfuric acid in the presence of 20–30 ml. of acetone per 100 ml. of solution, using starch as indicator. However, according to Lang,[24] starch does not give satisfactory results and it is better to use carbon tetrachloride or chloroform. He states that, in the presence of acetone, iodine dissolved in chloroform or carbon tetrachloride gives a brown color instead of violet, and at the end-point the change is from slightly yellow to colorless. Lang also used a medium 1N in hydrochloric acid.

Berg used the method only for the titration of iodides. Lang[24] states that arsenic(III) can also be titrated if the volume is kept small.

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[22] W. Böttger, *Newer Methods of Volumetric Chemical Analysis*, Chapman and Hall, London, 1938, p. 79.

[23] R. Berg, *Z. anal. Chem.*, 69, 369 (1926).

[24] Ref. 22, p. 80.

Titrations in Presence of Mercuric Salts: It has been shown by Hovorka and by Furman and his coworkers[25] (see also p. 219) that mercuric salts can exert a profound influence on the course of the iodate oxidation. Under conditions where the reaction is normally stayed at the production of free iodine, the latter is further reduced to iodide when a mercuric salt is present. This is due to a shifting of the equilibrium

$$I_2 \rightleftharpoons I^+ + I^-$$

to the right because of the complexing action of mercuric on iodide ions. Trivalent arsenic and antimony and hydrazine and its derivatives may be titrated in this way.

PRACTICAL SECTION

Preparation of Solutions:

0.1N Potassium Iodate: Weigh 5.351 g. of pure potassium iodate, which has been dried at 160–180°C., dissolve in distilled water, and make up to 1 liter. The purity of potassium iodate has already been considered (Vol. II, p. 54, and Vol. III, p. 234).

Iodine Monochloride: Dissolve 6.44 g. of potassium iodate and 10 g. of potassium iodide in 75 ml. of water in a glass-stoppered bottle, add 75 ml. of concentrated hydrochloric acid and 5 ml. of carbon tetrachloride. Add potassium iodate or iodide solution, shaking vigorously between each addition until only a very faint violet color remains in the solvent layer. Store in the dark when not in use.

Indicators: 0.2 per cent aqueous solutions of amaranth, brilliant ponceau 5R or naphthol blue black.

General Procedure[26] (a) Using an Immiscible Solvent as Indicator: Transfer 25 ml. of the solution to a 250 ml. glass-stoppered bottle or Erlenmeyer flask and dilute to about 50 ml. with water. Add an equal volume of concentrated hydrochloric acid and about 5 ml. of carbon tetrachloride or chloroform. Cool to room temperature.

Add 0.1*N* potassium iodate solution from a burette until the solution, which darkens at first owing to the formation of free iodine, lightens to pale brown. Stopper the vessel and shake vigorously; the organic solvent should acquire a violet color. Add small amounts of the titrant, shaking well after each addition, until the solvent is but faintly violet. Thereafter add the titrant a drop, or fraction of a drop, at a time, again shaking vigorously between each addition. The end-point is taken at the stage where the last trace of violet color disappears.

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[25] V. Hovorka, *Collection Czech Chem. Communs.*, **2**, 559 (1930); **3**, 285 (1931); *Chem. Listy*, **26**, 19 (1932); N. H. Furman and C. O. Miller, *J. Am. Chem. Soc.*, **59**, 152 (1937); I. C. Schoonover and N. H. Furman, *ibid.*, **55**, 3123 (1933).

[26] Ref. 22, p. 72.

It is important to remember that for many determinations the acid concentration should not fall below 3.5–4*N* at the end-point; hence, if a large amount of titrant is required, more hydrochloric acid should be added to maintain the above normality.

General Procedure (b) Using a Dyestuff as Indicator: Proceed as in the previous method but use a 250 ml. Erlenmeyer flask as container and do not add an organic solvent. Titrate until almost the whole of the iodine has disappeared, add 6–8 drops of indicator, and continue the titration until the color of the indicator is destroyed. If the indicator should be prematurely bleached as shown by lessening of its color, add a further 1–2 drops.

2. Direct Methods. ***Arsenic(III):*** Follow either procedure (*a*) or (*b*).

Notes: (1) The method has been applied to the determination of arsenic in glass,[27] insecticides, and fungicides.[28] Iron(III), copper, and most organic compounds do not interfere.

(2) *p*-Ethoxychrysoidine may be used as indicator in procedure (*b*), but 12 drops of a 0.1 per cent ethanolic solution are added in place of the irreversible dyestuff. One or two drops from the end-point, the red color changes to reddish purple. At this stage it is advisable to allow 10–20 seconds between each further addition to avoid all risk of overshooting the end-point. The end-point is marked by a change to orange. So far this indicator has only been applied to the titration of arsenite and isonicotinyl hydrazide (p. 464).

It is necessary to determine the blank value on each new batch of indicator. This may be as high as 0.2 ml. of 0.1*N* iodate when 12 drops of an ethanolic solution are used. When a few drops of arsenite solution are added, the indicator changes back to a faint pink after standing about 1 minute. On retitrating with iodate solution the color deepens at first before the end-point is reached.

(3) The acid concentrations recommended by different investigators vary considerably (e.g., Mutschin, 1.8–4.8*M*,[29] and Wilson, 3–6*M*).[27] However, those given above are known to work satisfactorily.

Antimony(III): There has been some disagreement about the correct conditions for this determination, although it has been stated that the same conditions may be used as for arsenic(III).[5] Smith and Wilcox[13] maintain that an end-point cannot be obtained when potassium antimonyl tartrate is titrated and an organic solvent is used to mark the end-point, although their own modification using a dyestuff as indicator is satisfactory. It is possible, however, that their acid concentration was too high, for other workers make no reference to experiencing similar difficulties.

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[27] H. N. Wilson, *Analyst*, **68**, 361 (1943).

[28] G. S. Jamieson, *Ind. Eng. Chem.*, **10**, 290 (1918).

[29] A. Mutschin, *Z. anal. Chem.*, **106**, 1 (1936).

Jamieson[8] states that he titrated antimony(III) compounds in the presence of "15–20" per cent of hydrochloric acid. His details for the determination of antimony in solders, type metals, and various alloys are more precise.

Mutschin[29] has commented on the lack of agreement among various writers concerning the optimum range of acidity. He found that at the end-point an acidity of 1.8–2.4N in hydrochloric acid gives good results; high results are obtained below this acidity and the maximum may only be exceeded when large amounts of antimony are present (greater than 21 ml. of 0.05M $SbCl_3$). Even in this case the acidity should not exceed 3.6N, for the end-point is then delayed and the titration must be done slowly. This difficulty may be overcome to some extent by first adding 2–5 ml. of 0.5M iodine monochloride. It may be concluded from Mutschin's findings that the general permissible range is 1.8–3.6N. Hammock, Brown, and Swift[30] also commented on the fact that the end-point is only precise within a narrow range of acid concentration (2.5–3.5N hydrochloric acid). Their findings are not very different from those of Mutschin, except that their lower limit is somewhat higher. They noted that at acidities less than 2.5N there was a tendency to overshoot the end-point owing to the slow rate of oxidation of iodine to iodine monochloride.

Procedure (*a*): Transfer 25 ml. of the solution to the container, add sufficient 6N hydrochloric acid to yield an acid concentration of 3N when the solution is diluted to 100 ml. (taking into account the acid already present in the antimony solution). Dilute to 100 ml. and add 5 ml. of organic solvent. Titrate with 0.1N potassium iodate solution in the usual way. If more than 25 ml. of iodate solution is required, add an amount of 6N hydrochloric acid equal in volume to the excess of titrant.

Note: Care must be taken to maintain the acid concentration between the prescribed limits. The above procedure, which is based on the recommendations of Hammock *et al.*,[30] ensures that the acidity is maintained between 2.4 and 3.5N.

Procedure (*b*) (for Potassium Antimonyl Tartrate): Follow the general procedure (p. 457) using indicator 184.

Determination of Antimony in Alloys (Hard Leads, Solders, Type Metals, and Similar Alloys):[8,13]

Procedure: Transfer 0.1–1.0 g. of metal to a 200 ml. flask, add 10 ml. of concentrated sulfuric acid, cover, and heat until the alloy is decomposed. When the precipitated lead sulfate is white, boil to expel sulfur dioxide and allow to cool. Add 15 ml. of water and 15 ml. of 1:1 hydrochloric acid, shake thoroughly, cool, and filter off the lead sulfate on a Gooch crucible. Wash the precipitate with a small amount of 1:1 hydrochloric acid. Transfer the filtrate to a stoppered flask, add 15 ml. of concentrated hydrochloric acid, cool, and add 6 ml. of organic solvent. Titrate with $0.1N$ potassium iodate solution and when the end-point is reached allow to stand for 10 minutes with occasional shaking to check if the iodine color returns.

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[30] E. W. Hammock, R. A. Brown, and E. H. Swift, *Anal. Chem.*, 20, 1048 (1948).

[31] G. S. Jamieson, *Ind. Eng. Chem.*, 11, 250 (1911).

Notes: (1) In some cases Jamieson recommends that the alloy be decomposed with hydrochloric acid and potassium chlorate. The excess acid is then partly neutralized with sodium hydroxide or ammonia solution and Sb(V) is reduced with sulfur dioxide. After the sulfur dioxide has been boiled out, the solution is cooled, slightly less than an equal volume of concentrated hydrochloric acid is added, and the titration completed as above.

(2) When very small amounts of antimony are present, 5 ml. of iodine monochloride solution should be added and the solution be allowed to stand for 5 minutes before titrating.

(3) If more than 25 ml. of titrant is needed, more hydrochloric acid should be added to ensure that there is not less than "12 per cent" of actual hydrochloric acid present when the end-point is reached.

(4) When arsenic is present it is precipitated and separated as the sulfide after filtering off lead sulfate. Air is then passed through the solution for 30 minutes to remove hydrogen sulfide and to reoxidize any iron(II) to iron(III).

Tin(II): According to Jamieson,[8,32] it is not necessary to take special precautions to avoid atmospheric oxidation because the titrant may be added rapidly in the initial stages of the titration.

Procedure: Follow the general procedure (*a*) but add the titrant rapidly with gentle rotation of the container until the iodine color reaches a maximum. Stopper the vessel, shake thoroughly, and complete the titration.

Tin (Metal):[8,32]

$$KIO_3 + Sn + 6HCl \longrightarrow SnCl_4 + KCl + ICl + 3H_2O$$

Procedure: Dissolve 3 g. of tin in 150 ml. of hydrochloric acid and add sufficient nitric acid to oxidize tin(II) to tin(IV). Add 3 g. of tartaric acid and dilute to 1 liter. Transfer an aliquot to the container and add 2 g. of high grade 30 mesh zinc. After 20 minutes or so, add 40 ml. of 1:2 hydrochloric acid. When the zinc has dissolved leaving metallic tin, add several milliliters of titrant, 10 ml. of concentrated hydrochloric acid, and a piece of platinum foil to facilitate the dissolution of the precipitated tin. Titrate while shaking thoroughly until all the tin has dissolved. Add 6 ml. of carbon tetrachloride and titrate to the end-point.

A blank determination is necessary.

Notes: (1) It is important to add sufficient titrant throughout the titration so that iodine or iodine monochloride is present at all times. Otherwise, the tin

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[32] G. S. Jamieson, *Ind. Eng. Chem.*, 8, 500 (1916).

metal may dissolve to yield nascent hydrogen and stannous chloride, which cause serious errors.

(2) The dissolution of tin, even in presence of platinum foil, is slow and the titration requires 30–45 minutes for its completion.

(3) Because the reaction is so slow, some workers prefer to boil the hydrochloric acid solution containing the precipitated tin until dissolution is complete and then to titrate the stannous tin so formed with iodate.[33]

(4) Jamieson also recommended strips of nickel (1 x 5.5 x 0.1 cm.) for the reduction of tin(IV) to tin(II). The solution was transferred to a 250 ml. Erlenmeyer flask fitted with a two-hole rubber bung. Two strips of nickel and 15 ml. of concentrated hydrochloric acid were added. A glass tube was inserted through one hole to within 1 cm. of the surface of the liquid and another through the other hole to just below the stopper. The flask was heated for 45 minutes on the steam bath while carbon dioxide was passed, and cooled in an ice bath; the solution was filtered through sea-sand and cotton into the titration vessel using suction. Carbon dioxide was led into the filter through a bent tube before starting filtration. The flask and filter were washed with a little 1:1 hydrochloric acid and the solution was titrated immediately. A blank was run for each new batch of nickel owing to its containing iron.

The method has been applied to the determination of tin in solder, type metals, bronze, and other alloys.[32,34]

(5) Ramsey and Blann[35] reduced with zinc and then added more hydrochloric acid and a little nickel or cobalt chloride solution to promote the redissolution of the tin. They adjusted the acidity to 1N, added a slight excess of 0.1N iodate solution while passing carbon dioxide, and back-titrated with thiosulfate because they found the oxygen error to be appreciable at the high acidity of the Andrews titration. They state that, if the stannous chloride solution is added to excess of potassium iodate solution, precise results are obtained even with 6N hydrochloric acid solutions without excluding air.

Ferrous Iron:

Procedure (a) Using an Organic Solvent:[15] Add 6 ml. of iodine monochloride solution, dilute to 50 ml., add 50 ml. of concentrated hydrochloric acid and 5 ml. of carbon tetrachloride, cool, and titrate with 0.1N potassium iodate solution.

Procedure (b) Using a Dyestuff as Indicator: Proceed as above but omit the solvent and use an ordinary 250 ml. Erlenmeyer flask to contain the solution. Titrate according to the general method (p. 457), using any of the three indicators.

Notes: (1) In the above titrations, Smith and Wilcox[13] noted that the normality of the iodate was 0.1009N when titrated against ferrous sulfate, which had been evaluated with standard permanganate or ceric sulfate, even though the normality was 0.1000N against pure arsenious oxide. It is recommended therefore that the iodate solution be standardized against iron as reference, otherwise low results are obtained.

(2) The titration may be done in the presence of many organic substances: for example, citric and tartaric acids, glycerol, ethanol, sodium oxalate, and filter paper do not interfere.

[33] J. W. Price, Tin Research Institute (England), private communication.

[34] J. H. van der Meulen, *Chem. Weekblad*, 45, 653 (1949).

[35] J. B. Ramsay and J. G. Blann, *J. Am. Chem. Soc.*, 56, 815 (1934).

Thallium:

Procedure (a):[36] Transfer 20 ml. of solution (0.25–0.30 g. Tl) to the titration vessel, add 60 ml. of concentrated hydrochloric acid and 5 ml. of organic solvent, and titrate with standard iodate solution.

Note: Swift and Garner[37] recommend that the solution be pretreated with 5 ml. of iodine monochloride. They state that the titration may be done at an acidity of 1–5*N* in hydrochloric acid for a range of 0.078–0.42 g. of thallium per 100 ml.

Procedure (b): Transfer 10 ml. of solution to an Erlenmeyer flask, add 40 ml. of concentrated hydrochloric acid, and dilute to 110 ml. Titrate with iodate, using indicator 184.

Iodide:

Procedure: Apply the general procedure (p. 456). The use of dyestuffs does not appear to have been attempted for this titration.

Note: Iodine and iodide in admixture may be determined by titrating free iodine with thiosulfate under the usual conditions, and then titrating the total iodine and iodide on a separate portion by the iodate procedure.

Andrews[5] believed that his method was inapplicable in the presence of bromides, because iodine monobromide imparted a reddish brown color to the solvent layer. Many later workers[38] have overcome this difficulty. Mutschin[38] recommends that the solution be saturated with potassium bromide. His procedure is as follows:

Dissolve the material (equivalent to 0.2–0.3 g. of potassium iodide) in the least amount of water, add 40 ml. of saturated potassium bromide solution, 20–30 ml. of concentrated hydrochloric acid, and then sufficient water to redissolve the precipitated salt (or sufficient to ensure that the salt is dissolved during the titration). Add 5 ml. of solvent and titrate with iodate.

Lang[38] explains the effect of bromide concentration as follows. Iodine bromide is partially dissociated so that it colors the organic solvent violet

$$2I^+ + 2Br^- \rightleftharpoons I_2 + Br_2$$

to red, and the Andrews titration is only possible if the dissociation is prevented. Lang found that for small concentrations of iodine (less than 30 mg. per 100 ml.), any amount of bromide could be present, but that for higher iodine concentrations there are two permissible limits of bromine concentration: a lower one which must not be exceeded and a higher one above which there is no interference. In the first case, the above equilibrium lies far to the left because of the very low concentration of bromide. In the second case, the I^+ ion forms a complex ion IBr_2^- which is not dissociated to any extent:

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[36] A. J. Berry, *Analyst*, 51, 137 (1926).

[37] E. H. Swift, and C. S. Garner, *J. Am. Chem. Soc.*, 58, 113 (1936).

[38] L. Michiels and B. Tougarinoff, *J. pharm. Belg.*, 15, 845 (1933); A. Mutschin, *Z. anal. Chem.*, 106, 1 (1936); R. Lang, *ibid.*, 106, 12 (1936).

$$I^+ + 2Br^- \rightleftharpoons IBr_2^-$$

and the first reaction is forced to the left. As the iodine concentration is lowered the two limits approach each other and finally merge at very low concentrations.

It is possible to carry out other titrations using the iodine bromide procedure,[3] and the acid concentration need only be low ($\simeq 0.5N$); however, the methods are of little practical importance, for each titration consumes 20–40 g. of potassium bromide.

Sulfurous Acid and the Sulfites:[8,39]

Procedure (*a*): Follow the general procedure (p. 456) exactly but cool the hydrochloric acid to 18°C. before it is added.

Notes: (1) This procedure serves for 22–63 mg. of SO_2. For larger amounts, place 10–15 ml. of iodine monochloride solution and the usual amount of hydrochloric acid in the container and add the sulfurous acid. Swirl the contents of the vessel, add the solvent, and titrate.

(2) When sulfites are to be titrated, weigh in short specimen tubes, drop into the acid solution, and stopper quickly to avoid loss of sulfur dioxide.

(3) The method has been applied by Haller[40] to the determination of sulfur dioxide in gaseous mixtures.

Procedure (*b*): Follow the general procedure exactly, using indicator 184.

Thiosulfate:

Procedure (*a*): Transfer 25 ml. of test solution to the titration vessel and add a mixture of 25 ml. of water and 50 ml. of concentrated hydrochloric acid, cooled below 18°C. Add the organic solvent and titrate immediately.

Procedure (*b*): Proceed exactly as above, but use indicator 184.

Notes:[8,41] (1) Tetrathionates may be determined in exactly the same way as thiosulfates; it is not necessary, however, to cool the acid before it is added.

(2) Dithionates react so slowly with iodate in the presence of hydrochloric acid that thiosulfates or tetrathionates may be determined in their presence.

Thiocyanate:

Procedures (*a*) *and* (*b*): Follow the general procedures (p. 456) exactly but titrate rapidly to prevent atmospheric oxidation at the high acidity.

Notes: (1) Hammock, Beavon, and Swift[42] state that a negative error is obtained which increases with the acid concentration. This error may be de-

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[39] G. S. Jamieson, *Am. J. Sci.*, **38**, 166 (1914).

[40] P. Haller, *J. Soc. Chem. Ind.*, **38**, 52T (1919).

[41] G. S. Jamieson, *Am. J. Sci.*, **39**, 639 (1915).

[42] E. W. Hammock, D. Beavon, and E. H. Swift, *Anal. Chem.*, **21**, 970 (1949).

creased by adding iodine monochloride which decreases the polymerization and decomposition of thiocyanate. Side reactions, e.g., formation of thionic acids, may be significant at lower acid concentrations. Their recommended conditions are as follows:

To 25–50 ml. of 0.015M thiocyanate, add 15 ml. of solvent and cool in an ice bath to less than 10°C. Add 5 ml. of previously cooled 0.5M iodine monochloride in 3M hydrochloric acid. Shake the flask until iodine passes into the solvent. Add sufficient 12M hydrochloric acid to give an acid concentration of 3.5M at the end-point. A small portion of acid should be first added round the neck of the flask and the stopper partly withdrawn to minimize the loss of iodine. Stopper the flask and shake. Titrate immediately with 0.1N potassium iodate solution.

(2) Gauguin[43] studied the oxidation of thiocyanate with iodate potentiometrically and concluded that the reaction proceeds through three stages:

$$5CNS^- + 6IO_3^- + 2H_2O + H^+ \longrightarrow 5SO_4^{2-} + 5HCN + 3I_2$$

The reaction between thiocyanate and iodine in an acid medium is so slow, however, that iodine is practically unattacked during the determination.

$$5HCN + 2I_2 + IO_3^- + H^+ \longrightarrow 5ICN + 3H_2O$$

$$2I_2 + 5Cl^- + IO_3^- + 6H^+ \longrightarrow 5ICl + 3H_2O$$

Hydrazine:

Procedure: Follow either general procedure (a) or (b). If the latter is used, indicators 184 and 185 are suitable.

Notes: Penneman and Audrieth[44] state that the acid concentration at the end-point should be 3–5N. There is a positive error if this is too low.[45] The temperature should preferably be above 30°C. when indicators 184 and 185 are used; the heat of dilution ensures this condition being fulfilled. They recommend this titration for the determination of hydrazine in the presence of ammonia and other basic substances.

(2) It is not possible to determine phenylhydrazine by the original Andrews methods, for it contains some extractable impurity which obscures the end-point.[8,46] However, it may be determined in exactly the same way as hydrazine by the Smith-Wilcox modification; indicator 184 is preferable in this titration. Haszeldine[46] found that indicator 185 was satisfactory if the hydrochloric acid concentration at the start of the titration was 6–7 N.

(3) Kurtenacker and Kubina[47] have determined semicarbazide by the Andrews method; the general procedure is applicable.

(4) Miller and Furman[48] have studied the titration of phenylhydrazine and semicarbazide at acidities of 3–6N in hydrochloric acid and at lower acidities in the presence of mercuric salts. The end-points were obtained potentiometrically and by using carbon tetrachloride. The latter was not very satisfactory at the lower acidities. They concluded, however, that Andrews' conditions gave the best results (using either a potentiometric or carbon tetrachloride end-point). In the titration of semicarbazide with carbon tetrachloride as indicator the solution must be very thoroughly shaken near the end-point. It was also noted that semicarbazide could be titrated in the presence of urea.

[43] R. Gauguin, *Anal. Chim. Acta*, **3**, 272 (1949).

[44] R. A. Penneman and L. F. Audrieth, *Anal. Chem.*, **20**, 1058 (1948).

[45] I. M. Kolthoff, *J. Am. Chem. Soc.*, **46**, 2009 (1924).

[46] G. S. Jamieson, *Am. J. Sci.*, **33**, 352 (1912); R. N. Haszeldine, University of Cambridge, private communication.

[47] A. Kurtenacker and H. Kubina, *Z. anal. Chem.*, **64**, 388 (1924).

[48] C. O. Miller and N. H. Furman, *J. Am. Chem. Soc.*, **59**, 161 (1937).

(5) Smith and Wheat[49] also used the iodate method for semicarbazide and some semicarbazones. The titration was not successful with thiocarbazide, furfuralsemicarbazone, or osazones.

(6) Aminoguanidonium salts and carbohydrazide may be determined[50] as follows: 50–100 mg. of sample is dissolved in 45 ml. of cold $7.5N$ hydrochloric acid, 15–20 ml. of chloroform is added, and the solution is titrated with $0.1N$ potassium iodate solution. Di- and triaminoguanidine, however, give erratic results, less than the expected amount of standard iodate solution being consumed.

Ascorbic Acid: Deshmukh and Barat[51] have studied the oxidation of ascorbic acid with potassium iodate. They recommend a two-stage titration. First the titration is done at a low acidity, ascorbic acid being oxidized to dehydroascorbic acid by iodine. The acidity is then increased and the titration is carried out in the usual way.

Procedure: To 10 ml. of approximately $0.1N$ ascorbic acid, add 5 ml. of $2N$ hydrochloric acid and 5–10 ml. of carbon tetrachloride. Titrate slowly with $0.1N$ potassium iodate solution until a faint permanent violet tint appears in the solvent after shaking. This represents the first stage of the oxidation. Add sufficient hydrochloric acid to bring the concentration to greater than $5N$ and continue the dropwise addition of titrant with vigorous shaking in between until the solvent becomes colorless.

Note: The titration need not be taken beyond the first end-point if made carefully; in this case the equivalent of the iodate is one sixth of the molecular weight. The second titration, however, serves as a check if the first end-point has been overshot.

Isonicotinyl Hydrazide: Domleo[52] found that the Andrews titration was unsatisfactory for isonicotinyl hydrazide because of the slow liberation of iodine, and no real end-point being obtained. He obtained good results, however, when *p*-ethoxychrysoidine[14] was used as indicator. The titration may be done in the presence of lactose and starch, which do not interfere.

Procedure: Dissolve 150 mg. of isonicotinyl hydrazide in 20 ml. of water, add 30 ml. of hydrochloric acid, and titrate with $0.05M$ KIO_3 while swirling the flask until about 90 per cent of the anticipated amount has been added. Add 12 drops of 0.1 per cent ethanolic *p*-ethoxychrysoidine and titrate slowly until the red color turns to orange. Continue the addition, allowing 30 seconds between drops until the orange color turns to yellow. Determine the blank value of the indicator. One ml. of $0.05M$ KIO_3 corresponds to 6.85 mg. of isonicotinyl hydrazide.

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[49] G. B. L. Smith and T. G. Wheat, *Ind. Eng. Chem., Anal. Ed.*, 11, 200 (1939).

[50] G. I. Keim, R. A. Henry, and G. B. L. Smith, *J. Am. Chem. Soc.*, 72, 4944 (1950).

[51] G. S. Deshmukh and M. G. Barat, *Z. anal. Chem.*, 145, 254 (1955).

[52] A. P. Domleo, *J. Pharm. and Pharmacol.*, 5, 117 (1953).

3. Indirect Methods. *Hydrogen Peroxide:*

Procedure: Run 30 ml. of 0.1N arsenious oxide solution (p. 43) from a burette into a stoppered vessel and add 10 ml. of 10 per cent sodium hydroxide solution. Add slowly 10 ml. of hydrogen peroxide solution (the commercial 20 vol. solution diluted 100 times) while shaking the container, and allow to stand for 2 minutes. Add 40 ml. of concentrated hydrochloric acid, shake well, and cool. Titrate the excess arsenious oxide with 0.1N potassium iodate solution in the usual way by procedure (*a*) or (*b*) (using amaranth as indicator).

Note: The method may be used when organic preservatives are present.[8,53]

Oxidizing Agents (*Lead, Manganese, or Barium Peroxide*):

Procedure:[8,54] Transfer the solid dioxide to the container, add 25 ml. of 0.1N potassium iodide solution and 25 ml. of concentrated hydrochloric acid. Stopper the bottle and shake until the solid has dissolved. Titrate the excess of iodide with 0.1N iodate solution (p. 461).

$$2PbO_2 + 2I^- + 8H^+ \longrightarrow 2Pb^{2+} + 2I^+ + 4H_2O$$

Notes: (1) Chlorates and chromates may be determined by similar procedures.[5] The reaction between iodide and chlorate should be allowed to proceed for 10 minutes in a closed flask in the presence of 1:2 hydrochloric acid. More than 3 moles of iodide should be used for each mole of chlorate. Slightly more than 3 moles should be used for every 2 moles of chromate. No mention is made of atmospheric oxidation, but Lang[55] believes this should be insignificant owing to the small excess of iodide present.

(2) Swift and Lee[56] determined iodate, permanganate, bromate, and chlorate in the presence of copper by adding excess of standard iodide to the neutral solution and then acidifying and titrating with a standard solution of the oxidant (cf. p. 355). The total amount of copper and oxidant is determined iodometrically.

Vanadium:[57] Vanadates are reduced to the quadrivalent state by potassium iodide in the presence of an excess of hydrochloric acid. The reduction must be done in an atmosphere of carbon dioxide. The residual iodide is back-titrated with iodate.

$$\begin{aligned} H_3VO_4 + HI + 2HCl &\longrightarrow VOCl_2 + \tfrac{1}{2}I_2 + 3H_2O \\ 2I_2 + HIO_3 + 5HCl &\longrightarrow 5ICl + 3H_2O \\ 2HI + HIO_3 + 3HCl &\longrightarrow 3ICl + 3H_2O \end{aligned}$$

Procedure: Transfer 25 ml. of the solution to the titration vessel and sweep out the air with a current of carbon dioxide. Add sufficient hydrochloric

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[53] G. S. Jamieson, *Am. J. Sci.*, 44, 150 (1917).

[54] R. S. Dean, *Chem. News*, 111, 2 (1915).

[55] Ref. 22, p. 91.

[56] E. H. Swift and T. S. Lee, *Ind. Eng. Chem., Anal. Ed.*, 14, 466 (1942).

[57] E. H. Swift and R. W. Hoeppel, *J. Am. Chem. Soc.*, 51, 1366 (1929).

acid (through which carbon dioxide has been passed for 15–20 minutes to sweep out dissolved air) to ensure that during the iodide-vanadate reaction the concentration will be 6–7*N*. Cool during this addition. Add a known excess of standard potassium iodide, mix, and allow to stand for 1–2 minutes. Add the organic solvent and titrate rapidly with standard iodate solution.

Notes: (1) If necessary, more acid should be added during the titration so that the final concentration of 6–7*N* is attained. At lower acidities there is partial reoxidation of V(IV) to V(V).

(2) A large excess of phosphoric acid has little effect. Arsenic(V) oxidizes iodide but is reoxidized by the iodate and therefore does not interfere. Tungstic oxide is held in solution by phosphoric acid and therefore has no effect. Iron(III) even in large amounts (1.0 g.) only causes a slight decrease in the titer.

4. Precipitation Methods (cf. p. 454).

Copper: Transfer 25 ml. of the solution (≃20–30 mg. of Cu) to a beaker, add a few drops of *N* sulfuric acid, and add 10–15 ml. of a freshly prepared saturated solution of sulfurous acid. Heat to boiling and add 10 per cent ammonium thiocyanate solution slowly and with constant stirring, from a burette, until further addition does not produce any color change (5–10 ml.). Add 3–4 ml. in excess. After 15 minutes, filter through a quantitative paper and wash with cold 1 per cent ammonium sulfate solution until free from thiocyanate.

Transfer the paper and precipitate to the titration vessel, add 30 ml. of concentrated hydrochloric acid, 20 ml. of water, and 5 ml. of chloroform. Titrate in the usual way.

Note: The method can be applied to the determination of copper in ores, alloys,[58] and insecticides.[8,59]

Mercury(I):[8,60] Dilute the mercury(I) solution to about 50 ml. in a beaker, and add 2 ml. of 2*N* hydrochloric acid. Stir thoroughly and allow to stand for at least 12 hours. Filter on a quantitative paper and wash with cold water. Transfer the paper and precipitate to the titration vessel, add 20 ml. of water and 30 ml. of concentrated hydrochloric acid, and shake well. Add the organic solvent and titrate with standard iodate.

Notes: (1) Mercury(II) may be determined likewise. In this case add an excess of 50 per cent phosphorous acid to the contents of the beaker after the addition of 2*N* hydrochloric acid. The precipitation, filtration, and titration follow the same course.

(2) Dried mercurous chloride reacts slowly with the titrant, and very thorough shaking is necessary. If possible, it should be finely powdered before being weighed.

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[58] G. S. Jamieson, L. H. Levy, and H. L. Wells, *J. Am. Chem. Soc.*, **30**, 760 (1908).

[59] G. S. Jamieson, *Chem. Met. Eng.*, **19**, 185 (1918).

[60] G. S. Jamieson, *Am. J. Sci.*, **33**, 349 (1912).

(3) Organic matter does not interfere, hence the method may be applied to the analysis of pharmaceutical materials.

Mercury(II):[8,61] Dissolve the compound in water containing 2 drops of concentrated hydrochloric acid and dilute to 50–75 ml. with water. Add 25 ml. of a solution containing 39 g. of ammonium thiocyanate and 29 g. of zinc sulfate per liter. Rub the beaker walls with a glass rod previously moistened with water, to facilitate its later rinsing, until crystallization starts, set aside for 5 minutes, and then stir vigorously for 1 minute. After 1 hour or more, filter on a 7 cm. paper supported on a Hirsch funnel, using gentle suction. Wash 4–5 times with a solution prepared by adding 5 ml. of reagent to 450 ml. of water. Drain gently, transfer the paper and precipitate ($HgZn(CNS)_4$) to the titration vessel, and add 10 ml. of a cooled mixture of 10 ml. of water and 35 ml. of hydrochloric acid. Add the organic solvent and titrate with standard iodate solution.

Notes: (1) A certain amount of free acid is necessary to ensure quantitative precipitation. It should not exceed 5 per cent. Excess may be neutralized with sodium hydroxide solution, but ammonia solution should not be used because of the solvent action of ammonium salts on the precipitate.
(2) If more than 50 ml. of iodate solution is required a further 10–15 ml. of concentrated hydrochloric acid should be added.
(3) Cadmium, cobalt, copper, bismuth, manganese, and mercury(I) interfere by forming insoluble compounds. Small amounts of nickel can be tolerated.
(4) The method has been applied to the determination of mercury in various pharmaceutical preparations.

Zinc:[8,62] Proceed exactly as in the determination of mercury but use a reagent containing 39 g. of potassium thiocyanate and 27 g. of mercuric chloride per liter. Transfer the precipitate to the filter and wash with a solution containing 5 ml. of precipitating reagent to 450 ml. of water and complete the determination as for mercury.

Notes: (1) Interferences are the same as with the mercury determination. Ferric iron should be reduced first with sulfurous acid.
(2) The determination has been applied to the analysis of commercial zinc arsenite. Arsenic(III) does not interfere with the precipitation.

Sulfides: Dean[63] has applied the Andrews method to the titration of heavy metal sulfides, e.g., CdS, ZnS, PbS.

$$3CdS + 3IO_3^- + 12H^+ \longrightarrow 3Cd^{2+} + 2S + H_2SO_4 + 3I^+ + 5H_2O$$

One third of the sulfide sulfur is converted to sulfate and the rest to free sulfur.

Procedure: Transfer the precipitate to the vessel and add immediately nearly the whole of the expected amount of standard iodate solution and sufficient hydro-

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[61] G. S. Jamieson, *Ind. Eng. Chem.*, **11**, 296 (1919).
[62] G. S. Jamieson, *J. Am. Chem. Soc.*, **40**, 1036 (1918).
[63] R. S. Dean, *J. Am. Chem. Soc.*, **37**, 1134 (1915).

chloric acid to give an 8.5–10.5N acid solution. Complete the titration in the usual way. Alternatively, add an excess of standard iodate solution and back-titrate with standard iodide solution.

Note: The method appears to be satisfactory for the divalent metal sulfides. However, with antimony and arsenic sulfides the oxidation process appears to be erratic. With antimony sulfide the oxidation mechanism varies according to the concentration, and with arsenious sulfide only two thirds of the anticipated amount of iodate is consumed. No explanation is offered to account for this phenomenon. Hence the method is not to be recommended for these two particular sulfides.

5. Other Determinations.

Molybdenum: Molybdenum may be determined[8,64] by passing the solution (as molybdate) through a Jones reductor into a solution containing iodine monochloride and hydrochloric acid. The solution is then titrated with standard iodate solution.

Selenium: Lang[65] attempted unsuccessfully to determine selenium produced by reduction with sulfurous acid. He treated with iodine monochloride and titrated after 1 hour, but obtained only 95 per cent recoveries owing to the remainder being in a nonattackable form. Willis[66] determined selenium in copper by precipitating with metallic iron and then titrating with standard iodate solution. The reaction is assumed to be

$$Se + KIO_3 + 6HCl \longrightarrow SeCl_4 + 3H_2O + KCl + ICl$$

Selenocyanide can be titrated satisfactorily after treating with iodine monochloride.[67] The reaction proceeds:

$$SeCN^- + IO_3^- + H^+ \longrightarrow SeO_3^{2-} + I^+ + HCN$$

Suseela[68] has determined selenium in selenites by treating with a known excess of hydrazine hydrosulfate and titrating the excess with standard iodate solution. She refluxes for 15 minutes in the presence of 2–3N hydrochloric acid to precipitate selenium as the element, filters on a Gooch crucible, dilutes the filtrate to 500 ml., and titrates the excess hydrazine by the Andrews method, which was preferred to the Lang cyanide titration. It is suggested that tellurium might be determined likewise.

Aryl diselenides may be titrated provided that the acid concentration is maintained at 5.0–5.5N at the end-point.[69] The reactions are believed to proceed as follows:

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[64] G. S. Jamieson, *J. Am. Chem. Soc.*, **39**, 246 (1917).

[65] R. Lang, *Z. anorg. Chem.*, **142**, 280 (1925).

[66] U. F. Willis, *Analyst*, **67**, 219 (1942).

[67] Ref. 22, p. 90.

[68] B. Suseela, *Z. anal. Chem.*, **147**, 13 (1955).

[69] M. D. McCullough, T. W. Campbell, and N. J. Krilanovich, *Ind. Eng. Chem., Anal. Ed.*, **18**, 638 (1946).

$$R_2Se_2 + 6ICl \longrightarrow 2RSeCl_3 + 3I_2$$

$$2I_2 + IO_3^- + 6H^+ + 5Cl^- \longrightarrow 5ICl + 3H_2O$$

Procedure: Titrate 1 ml. of 1.5*M* potassium iodide in 50 ml. of 12*N* hydrochloric acid with standard potassium iodate in the presence of 5 ml. of carbon tetrachloride until the latter just becomes colorless. Add 25 ml. of 12*N* hydrochloric acid and the weighed sample of the diselenide. Shake and titrate in the usual way with standard iodate solution until the solvent layer is colorless.

Note: It is suggested that a small amount of side reaction may take place owing to oxidation of diselenide to selenic acid; the results are sometimes 0.5–1 per cent low.

Sodium Hypochlorite: Sodium hypochlorite may be determined[70] by treating with an excess of standard arsenious oxide, thiosulfate, or iodide solution. The acidity is then adjusted and the excess of standard reductant is titrated with iodate.

Notes: (1) When thiosulfate or iodide is used, it is recommended that the solution be cooled in ice before acidification.

(2) Small amounts of chlorate or nitrate do not interfere with the arsenite method. Chlorate interferes in the thiosulfate and iodide methods.

Carbon: Carbon as graphite, activated carbon, or charcoal may be determined[71] by decomposing with potassium iodate and phosphoric acid at a temperature of more than 250°C., distilling the liberated iodine into standard arsenious oxide solution in an atmosphere of carbon dioxide and then back-titrating with potassium iodate.

6. The Iodine–Cyanide Method.[21,26] ***General Procedure:*** Transfer the neutral solution to a long narrow-necked flask (e.g., a volumetric flask) which must be used to minimize the volatilization of hydrocyanic acid. Acidify with an equal volume or, in any case, with at least 50 ml. of 2.5*N* hydrochloric acid. Add 6–8 ml. of 0.5*N* potassium cyanide solution and some starch indicator. Titrate with standard iodate solution until the blue color is discharged.

Alternatively add sufficient sulfuric acid to bring the concentration to 2*N* and add 1–2 g. of sodium chloride per 100 ml. of solution.

When only small quantities of test substances are present (with the exception of iodine and iodides), add a few milliliters of iodine monochloride solution before the titration, followed by a further amount of potassium cyanide solution (for x ml. of ICl add $x + 6$ ml. of KCN). Alternatively add solid iodine cyanide, for which an addition of 5 ml. of 0.5*N* potassium cyanide will suffice before the titration.

Arsenic(III) and Antimony(III): Follow the general procedure above.

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[70] J. R. Lewis and R. F. Klockon, *J. Am. Chem. Soc.*, **50**, 3243 (1928).

[71] T. Kiba, S. Ohashi, T. Tagaki, and Y. Hirose, *Japan. Analyst*, **2**, 446 (1953).

Notes: (1) The hydrolysis of antimony salts may be prevented by adding tartrate or sodium pyrophosphate, or by maintaining the concentration of hydrochloric acid not lower than 1.6*N*.

(2) Arsine may be determined[72] as follows: Transfer 10 ml. of iodine monochloride solution and 50–100 ml. of 2.8*N* hydrochloric acid to a flask of about 500 ml. capacity filled with a ground-in capillary cock. Evacuate the flask, draw in the gas, and shake for several minutes. Suck in some water, and add 1 g. of potassium cyanide and starch. Titrate with standard iodate solution.

$$AsH_3 + 2IO_3^- + 2HCN \longrightarrow AsO_4^{3-} + 2ICN + H^+ + 2H_2O$$

(3) Very small amounts of elementary arsenic can be titrated with iodate solution after being dissolved in iodine monochloride.[73]

Tin(II):[55] When stannous tin is titrated there are two stages in the reaction. The first stage is the point where all the stannous salt has been oxidized and the blue color then appears:

$$3Sn^{2+} + IO_3^- + 6H^+ \longrightarrow Sn^{4+} + I^- + 3H_2O$$

The second stage, marked by the disappearance of the blue color, is the point where all the iodide is completely oxidized:

$$2I^- + IO_3^- + 3HCN + 3H^+ \longrightarrow 3ICN + 3H_2O$$

The total reaction is represented by

$$2Sn^{2+} + IO_3^- + HCN + 5H^+ \longrightarrow 2Sn^{4+} + ICN + 3H_2O$$

Since atmospheric oxidation can occur if the titration is done slowly, it is best to add the iodate solution rapidly until the blue color appears. After this point there is no fear of atmospheric oxidation and the titration can be carried out slowly until the blue color disappears.

Procedure: Follow the general procedure but run in the standard iodate rapidly until the blue color appears. Thereafter continue the titration as usual.

Note: Antimony(III) and tin(II) can be determined together by proceeding as above (except that it is preferable to add the potassium cyanide after the blue color appears). The sum of the iodine cyanide and antimony(V) is then determined by adjusting the acidity, adding potassium iodide, and titrating with thiosulfate.

Copper:[55] Treat the ammoniacal solution of the copper salt (approximately 50 ml.) with 0.5*N* potassium cyanide solution until colorless. Add 2.5*N* hydrochloric acid using 5–10 ml. more than is necessary to precipitate cuprous cyanide permanently. Add 5 ml. of iodine monochloride (the precipitate then dissolves) followed by 20–30 ml. of 1:1 hydrochloric acid. Add starch indicator and titrate with iodate solution.

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[72] H. Kubina, *Z. anal. Chem.*, **76**, 39 (1929).

[73] J. Gangl and J. V. Sánchez, *Z. anal. Chem.*, **98**, 81 (1934).

Note: The method can be used for the analysis of white metals. Heavy metals (Bi, Sb, Sn, Zn, Cd, Fe) are kept in solution by the addition of sodium pyrophosphate and do not interfere.

Hydrazine: Follow the general procedure. It is better, however, to titrate drop by drop rather than to add the initial amount fairly rapidly.

Note: Hydrazine and hydroxylamine may be determined in admixture provided that not more than 0.07 g. of $NH_2OH{\cdot}HCl$ per 150 ml. is present. Hydrazine is determined by the above method but a sulfuric acid medium is used. Iodine cyanide is then removed and hydroxylamine is determined by Raschig's method based on reduction of ferric ammonium sulfate and back-titration with permanganate solution.[74]

Thiocyanate: Follow the general method but ensure that the acidity is about 1.5N in hydrochloric acid. Add excess of standard iodate solution rapidly and back-titrate with a standard arsenite solution.

Notes: (1) Atmospheric oxidation is pronounced, hence it is necessary to use the back-titration procedure. A direct titration can be carried out, however, if the thiocyanate solution is pretreated with iodine monochloride or iodine cyanide.

(2) The method has been applied to the analysis of polysulfides by treating with potassium cyanide to form thiocyanate. The latter is then determined as above, after the iodine monochloride pretreatment.[75]

Iodides: Follow the general method.

Notes: (1) Various difficultly soluble iodides, e.g., cuprous, lead, silver, and mercuric iodides, may be determined by suitable modifications. The original paper[76] should be consulted for working details.

(2) For small amounts of iodide (10 ml. of 0.1M) the blue color disappears very slowly and the titration takes 3 minutes. In the presence of bromide the reaction is even slower; the end-point is nonexistent if the amount is excessive. However, when organic solvents are used, very sharp end-points are obtained and this modification is recommended for the determination of traces of iodide in bromides. Even 0.1 mg. of iodide can be titrated in 100 ml. of solution to an accuracy of 1 per cent.[77]

Cadmium and Bismuth: Berg and Wurm[78] developed methods for the determination of cadmium and bismuth based on precipitation as β-naphthoquinoline cadmium iodide, $(C_{13}H_9N_2)H_2(CdI_4)$ and 8-hydroxyquinoline bismuth iodide $(C_9H_7ON)H(BiI_4)$. The iodide in the precipitates is finally titrated by the iodine cyanide or iodo-acetone method.

Cadmium. Procedure: Add to the test solution (cadmium sulfate), 50 ml. of 2N sulfuric acid, 50 ml. of 10 per cent sodium tartrate solution, and sufficient of a 2.5 per cent solution of β-naphthoquinoline in 0.5N sulfuric acid. Add some drops of a dilute solution of sulfurous acid and a slight excess of 0.2N potassium iodide solution. Dilute to about 150 ml. with water.

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[74] F. Raschig, *Ann.*, **241**, 191 (1887).

[75] J. González Carreró, *Anales real Soc. españ. fís. y quím. (Madrid)*, **45B**, 73 (1949); *Chem. Abstr.*, **44**, 8283 (1950).

[76] R. Lang, *Z. anorg. Chem.*, **142**, 229 (1925).

[77] I. M. Kolthoff, *Mikrochemie*, **3**, 75 (1925); *Pharm. Weekblad*, **62**, 878 (1925).

[78] R. Berg and O. Wurm, *Ber.*, **60**, 1664 (1927).

After 20 minutes, filter, suck as dry as possible, and wash with a freshly prepared solution of 10 ml. of the 2.5 per cent β-naphthoquinoline solution diluted to 90 ml. with water and 10 ml. of 0.2N potassium iodide. For the first 2–3 washes add 2–3 ml. of 0.2N potassium iodide solution to this wash solution. Suck the precipitate dry, decompose with 20 ml. of 2N sodium hydroxide solution, and just acidify. Adjust the acidity to 0.6N and titrate the iodide, using either Berg's or Lang's procedure.

Notes: (1) Cobalt, nickel, manganese, zinc, iron(II), chromium(III), and aluminum (as sulfates) do not interfere. A slight modification is necessary when tin and antimony are present.

(2) Pass and Ward[79] have applied this method to the determination of cadmium in zinc ores and spelter. They complete the determination by Lang's procedure.

Bismuth. Procedure: Add an excess of 5 per cent 8-hydroxyquinoline in 0.2N sulfuric acid to the slightly acid (nitric or sulfuric acid) test solution, followed by 0.1N potassium iodide solution added dropwise until the precipitate conglomerates. Filter immediately and wash with a solution composed of 50 ml. of 2N sulfuric acid, 25 ml. of 0.1N potassium iodide, 1.8 g. of 8-hydroxyquinoline, and a few crystals of hydrazine sulfate made up to 1 liter. Suck the precipitate dry, dissolve in 1.2N hydrochloric acid, and titrate with iodate solution by either Lang's or Berg's procedure.

Notes: (1) Cadmium, iron(II), nickel, cobalt, manganese, zinc, chromium(III), aluminum, magnesium, and arsenic(III) do not interfere. By suitable modification the method may be operated in the presence of copper, iron(III), antimony, and tin. Mercury, silver, lead, thallium, and large amounts of chloride interfere.

Even less than 1 mg. of bismuth may be determined satisfactorily.

(2) Kolthoff and Griffiths[80] found that low results were obtained when the chloride concentration exceeded 0.08N. A solution 1N to nitric, sulfuric, or perchloric acid was satisfactory. They found it preferable to titrate the excess of iodide in the filtrate; Andrews' method was preferred to Lang's method.

(3) Bismuth may be determined similarly after precipitation as caffeine tetraiodobismuthate.[81]

Other Determinations: Titanium and vanadium, after passing through a cadmium reductor, and tungsten, after reduction with a liquid lead amalgam, can be determined by the iodine-cyanide method.[82] Vanadium can also be determined after reduction with sulfurous acid.[83] Selenium as selenite may be determined[84] by reducing with an excess of standard hydrazine sulfate solution and back-titrating with standard iodate.

The original papers should be consulted for details.

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[79] A. Pass and A. M. Ward, *Analyst*, 58, 667 (1933).

[80] I. M. Kolthoff and F. S. Griffith, *Mikrochim. Acta*, 3, 46 (1938).

[81] R. S. Beale and G. C. Chandlee, *Ind. Eng. Chem., Anal. Ed.*, 14, 43 (1942)

[82] *Ref.* 22, p. 94.

[83] A. J. Berry, *Analyst*, 59, 736 (1934).

7. The Iodo-acetone Method (cf. p. 455).

Iodides:[23] Transfer the test solution to an Erlenmeyer flask, add 20–30 ml. of acetone followed by sufficient 1:1 sulfuric acid to give an acidity of 2–2.5*N* when the solution is diluted to 100 ml., which should be approximately the volume at the end-point. Add starch indicator and titrate dropwise with iodate solution at such a speed that the starch-iodine tint which is brownish in the early stages becomes pure blue near the end-point. The latter is marked by a change from blue to colorless.

Notes: (1) According to Lang,[24] better end-points are obtained when organic solvents are used in place of starch.

(2) Vorob'ev[85] states that the accuracy is increased if the titration is started at an acidity of 2.5*N* in sulfuric acid and is not allowed to fall below 1*N*.

(3) Berg and Wurm[78] also use the iodo-acetone method to complete the bismuth and cadmium determinations (p. 471).

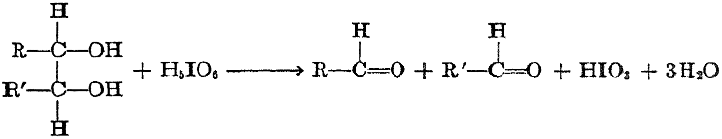
[84] R. Lang, *Z. anorg. Chem.*, 142, 280 (1925).

[85] A. S. Vorob'ev, *Zhur. Anal. Khim.*, 4, 200 (1949).

CHAPTER XI

OXIDATION OF ORGANIC COMPOUNDS WITH PERIODATE

1. The Malaprade Reaction. The use of periodic acid and periodates for the selective oxidation of organic compounds having hydroxyl groups attached to adjacent carbon atoms was introduced in 1928 by Malaprade.[1] The selectivity of periodic acid resembles that of lead tetraacetate and distinguishes these oxidizing agents from others for use with organic compounds. The reaction takes place in a few minutes at room temperature in weakly acid, neutral, or weakly basic solution. The α-diol is oxidized with the cleavage of the bond between the carbon atoms holding the hydroxyl groups and with the removal of two protons and two electrons; the periodate is reduced to iodate. The reaction may be written in the general form:



$$\begin{matrix} \text{R—CH—OH} \\ | \\ \text{R}'\text{—CH—OH} \end{matrix} + H_5IO_6 \longrightarrow \text{R—}\overset{\text{H}}{\overset{|}{\text{C}}}\text{=O} + \text{R}'\text{—}\overset{\text{H}}{\overset{|}{\text{C}}}\text{=O} + HIO_3 + 3H_2O$$

where R and R′ may denote hydrogen atoms as well as organic radicals. The simple monoalcohols are not oxidized appreciably under the conditions at which the α-diols are oxidized.

Carbonyl compounds having a carbonyl group adjacent to a carbon atom holding a hydroxyl group, or adjacent to another carbonyl group, react with periodic acid like the α-diols; the carbonyl group is oxidized to the carboxyl group.[2]

Periodic acid and periodates, therefore, react with α-ketols, α-diketones, α-ketone aldehydes, α-hydroxyaldehydes, and the αdialdehyde, glyoxal. Typical examples of these reactions are given in the following equations:

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[1] L. Malaprade, *Compt. rend.*, **186**, 382 (1928); *Bull. soc. chim. France*, [4] **43**, 683 (1928).

[2] P. Fleury and J. Lange, *Compt. rend.*, **195**, 1395 (1932), *J. pharm. chim.*, (8) **17**, 409 (1933); L. Malaprade, *Bull. soc. chim. France*, (5) **1**, 833 (1934); P. W. Clutterbuck and F. Reuter, *J. Chem. Soc.*, **1935**, 1467.

$$\underset{\text{acetoin}}{CH_3{-}CO{-}CHOH{-}CH_3} + H_5IO_6 \longrightarrow CH_3COOH + CH_3CHO + HIO_3 + 2H_2O$$

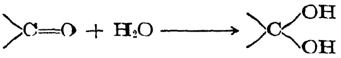
$$\underset{\text{diacetyl}}{CH_3{-}CO{-}CO{-}CH_3} + H_5IO_6 \longrightarrow 2CH_3COOH + HIO_3 + H_2O$$

$$\underset{\text{pyruvic aldehyde}}{CH_3{-}CO{-}CHO} + H_5IO_6 \longrightarrow CH_3COOH + HCOOH + HIO_3 + H_2O$$

$$\underset{\text{glycolic aldehyde}}{CH_2OH{-}CHO} + H_5IO_6 \longrightarrow HCHO + HCOOH + HIO_3 + 2H_2O$$

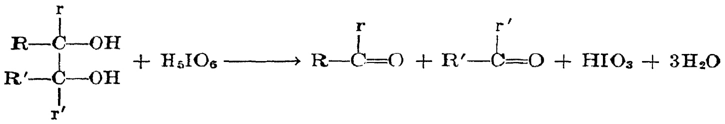
$$\underset{\text{glyoxal}}{CHO{-}CHO} + H_5IO_6 \longrightarrow 2HCOOH + HIO_3 + H_2O$$

The reactions of carbonyl compounds may be interpreted as proceeding through the hydration of the carbonyl group to give the α-diol structure:



$$>C{=}O + H_2O \longrightarrow >C{<}^{OH}_{OH}$$

If the carbonyl group is considered in this manner, the Malaprade reaction can be written in the general form:



$$\begin{array}{c} r \\ | \\ R{-}C{-}OH \\ | \\ R'{-}C{-}OH \\ | \\ r' \end{array} + H_5IO_6 \longrightarrow R{-}\overset{\displaystyle r}{\overset{|}{C}}{=}O + R'{-}\overset{\displaystyle r'}{\overset{|}{C}}{=}O + HIO_3 + 3H_2O$$

in which r and r′ are hydrogen atoms or hydroxyl groups. The simple monoaldehydes and ketones are not oxidized appreciably by periodic acid under the conditions at which the Malaprade reaction takes place.

Polyhydroxy compounds like glycerol, erythritol, and arabitol are oxidized to formic acid and 2 moles of formaldehyde. The reaction may be considered to take place stepwise through the hydroxyaldehydes, as for example:

$$\underset{\text{glycerol}}{CH_2OH{-}CHOH{-}CH_2OH} + H_5IO_6 \longrightarrow \underset{\text{glycolic aldehyde}}{CH_2OH{-}CHO} + HCHO + HIO_3 + 3H_2O$$

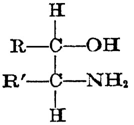
$$\underset{\text{glycolic aldehyde}}{CH_2OH{-}CHO} + H_5IO_6 \longrightarrow HCHO + HCOOH + HIO_3 + 2H_2O$$

The overall, general equation can be written:

$$CH_2OH—(CHOH)n—CH_2OH + (n+1)H_5IO_6 \longrightarrow 2HCHO + nHCOOH + (n+1)HIO_3 + (2n+3)H_2O$$

It is of interest to note here that α-diols when oxidized by periodic acid yield carbonyl compounds only, whereas α-carbonyl alcohols, and therefore polyhydroxy compounds, when oxidized yield in addition carboxylic acids. This fact is utilized analytically.

In addition to its reaction with organic compounds having oxygen atoms of the hydroxyl or carbonyl group attached to adjacent carbon atoms, periodic acid reacts rapidly with α-amino alcohols in which the amine group is primary or secondary.[3] The reaction differs from the oxidation of compounds having the α-diol structure in the production of ammonia. The reaction can be written in the general form:



$$\begin{array}{c} H \\ | \\ R—C—OH \\ | \\ R'—C—NH_2 \\ | \\ H \end{array} + H_5IO_6 + H^+ \longrightarrow RCHO + R'CHO + NH_4^+ + HIO_3 + 2H_2O$$

Typical examples of the reaction are:

$$\underset{\text{ethanolamine}}{CH_2OH—CH_2NH_2} + H_5IO_6 + H^+ \longrightarrow 2HCHO + NH_4^+ + HIO_3 + 2H_2O$$

$$CH_2OH—\underset{\text{serine}}{CH(NH_2)}—COOH + H_5IO_6 + H^+ \longrightarrow HCHO + OHC—COOH + NH_4^+ + HIO_3 + 2H_2O$$

The oxidation of α-amino alcohols in which the amine group is tertiary proceeds only very slowly. α-Diamines, α-amino acids, and acylated derivatives of α-amino alcohols likewise are oxidized only very slowly. Several amino acids which do not have the α-amino alcohol structure, but which are obtained in protein hydrolyzates, are oxidized by periodic acids without, however, the production of ammonia. Tryptophan rapidly reduces periodic acid with the formation of an insoluble product. Methionine and cystine also react rapidly probably through the oxidation of the sulfur in these compounds.

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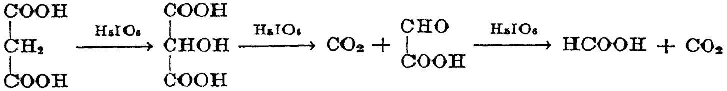
[3] B. H. Nicolet and L. A. Shinn, *J. Am. Chem. Soc.*, 61, 1615 (1939); P. Fleury, J. Courtois, and M. Grandchamp, *Bull. soc. chim. France*, 1949, 88.

After prolonged periods of contact or at elevated temperatures, periodic acid and periodates are less selective as oxidizing agents. Compounds having active hydrogen atoms are oxidized slowly at room temperatures, rapidly at elevated temperatures.[4] Malonic acid, for example, is oxidized to formic acid and carbon dioxide. The probable course of the reaction is:



$$\begin{array}{l}COOH\\|\\CH_2\\|\\COOH\end{array} \xrightarrow{H_5IO_6} \begin{array}{l}COOH\\|\\CHOH\\|\\COOH\end{array} \xrightarrow{H_5IO_6} CO_2 + \begin{array}{l}CHO\\|\\COOH\end{array} \xrightarrow{H_5IO_6} HCOOH + CO_2$$

In this process, the first step appears to be the slowest. Acetoacetic acid yields 1 mole each of acetic acid, formic acid, and carbon dioxide. Malic acid yields 2 moles of formic acid and 1 mole of carbon dioxide.

The carboxylic acid group, although it might be considered to consist of a carbonyl and hydroxy grouping, is not normally oxidized even though an hydroxyl group is attached to the adjacent carbon atom.[5] Glycolic, lactic, and oxalic acids are not oxidized at room temperatures even after several hours. α-Keto acids are oxidized very slowly at room temperature with an excess of periodate. Glyoxylic and mesoxalic acids are the most reactive of these acids and in basic solutions with an excess of periodate they yield carbon dioxide quantitatively in 10 minutes, but even the reactions of these acids are slower than those of α-diols and α-ketols with periodic acid. By a proper selection of conditions, e.g., lower temperatures or acidic solutions, periodic acid can be made to oxidize α-diols and α-ketols quantitatively without oxidizing the carboxylic acids.

At 100°C., α-hydroxy, α-keto, and α-amino acids are oxidized fairly rapidly by periodate.[6] It is interesting to note that the oxidation apparently proceeds according to the usual Malaprade reaction with the carboxyl group behaving like a hydroxy group, rather than through the dehydrogenation path of most oxidizing agents. This is shown by the oxidation of lactic acid at 100° to 1 mole of acetaldehyde and 1 mole of carbon dioxide rather than to pyruvic acid. The acetaldehyde is very slowly oxidized at this temperature to methanol and formic acid; the methanol is further oxidized to formaldehyde, then to formic acid, and finally to carbon dioxide. Pyruvic acid, on the other hand, is oxidized at 100° to acetic acid and carbon dioxide; this is also in line with the usual Malaprade reaction, for the acetic acid is apparently not oxidized even at 100°. The same is true of propionic acid. Dihydroxymaleic acid is oxidized to oxalic acid,[7] and citric acid is oxidized to 2 moles of formic acid and 4 moles of carbon dioxide.

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[4] C. F. Heubner, S. R. Ames, and E. C. Bubl, *J. Am. Chem. Soc.*, **68**, 1621 (1946); P. Fleury and J. Courtois, *Compt. rend.*, **223**, 633, (1946), *Bull. soc. chim. France*, **1947**, 358; *ibid.*, **1948**, 190.

[5] D. B. Sprinson and E. Chargaff, *J. Biol. Chem.*, **164**, 433 (1946).

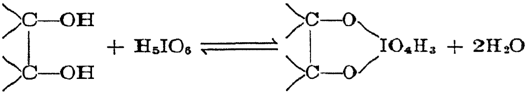
[6] P. Fleury and S. Boisson, *Compt. rend.*, **204**, 1264 (1937); P. Fleury and S. Boisson, *J. pharm. chim.*, **30**, 145, 307 (1939), *Compt. rend.* **208**, 1509 (1939); D. B. Sprinson and E. Chargaff, *J. Biol. Chem.*, **164**, 433 (1946).

At 100°, the simple alcohols, ketones, and aldehydes are slowly oxidized by periodate. Methanol is oxidized to formaldehyde. Formaldehyde is oxidized to formic acid; acetaldehyde to formic acid and methanol. Acetone is oxidized to acetic acid and formaldehyde; diethyl ketone, probably to propionic acid and ethanol. Formic acid is slowly oxidized to carbon dioxide but there is apparently no reaction with acetic and propionic acids. The oxidation of organic compounds with periodic acid and periodate at high temperatures is a complex process and is generally not used analytically.

Another factor which apparently influences the specificity of periodate oxidations of complex materials is light.[8] Jackson and Hudson[9] observed that, in the oxidation of cellulose, more than 1 mole of periodate is consumed per glucose unit. Values as high as 1.86 were reported for filter paper. Head[8] repeated these experiments in the absence of light and found that the reaction ceases when 1 mole of periodate is consumed per glucose unit. Even after 41 days only 1.06 mole of periodate is consumed. On the other hand, when the reaction mixture is kept in bright daylight, all of the excess periodate present in the mixture is eventually consumed.

An excellent review of the use of the Malaprade reaction in organic chemistry especially with regard to synthetic and structural studies is presented by Jackson.[10] Analytical applications of periodic acid and periodates are reviewed by Smith.[11]

2. Mechanism of the Malaprade Reaction. Criegee[12] attributed the selectivity of periodic acid as an oxidizing agent to its ability to form cyclic esters with the α-diols. The mechanism which he postulated can be expressed by the following equations:



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[7] Gunnar Lundblad, *Arkiv Kemi, Mineral. Geol.*, **25A**, 42 pp. (1947), *Chem. Abstr.*, **42**, 7249c (1948).

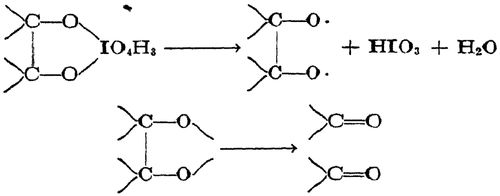
[8] F. S. H. Head, *Nature* **165**, 236 (1950).

[9] E. L. Jackson and C. S. Hudson, *J. Am. Chem. Soc.*, **59**, 2049 (1937).

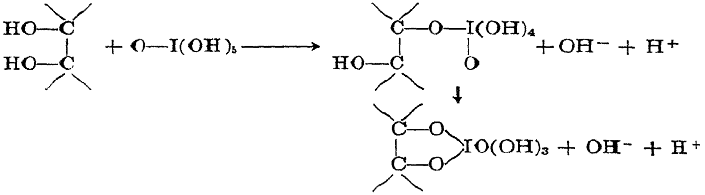
[10] E. L. Jackson, in *Organic Reactions*, Vol. II, Chapt. 8, Adams *et al.*, eds., Wiley, New York, 1944; cf. J. M. Bobbitt, *Advances in Carbohydrate Chem.*, **11**, 1 (1956).

[11] G. F. Smith, *Analytical Applications of Periodic Acid and Iodic Acid and Their Salts*, G. F. Smith Chemical Co., Columbus, 1950.

[12] R. Criegee, *Sitzber. Ges. Beförder. ges. Naturw. Marburg*, **69**, 25 (1934), *Chem. Abstr.*, **29**, 6820 (1935); *Angew. Chem.*, **50**, 153 (1937).



Price and Kroll[13] and Price and Knell[14] studied the rate of reaction of pinacol, ethylene glycol, *trans*-cyclohexene glycol, and *cis*-cyclohexene glycol with periodate over a considerable range of pH. The reaction rate at a given pH agrees with that for a second order reaction, i.e., first order with respect to each of the reactants, periodate and glycol. The reaction rate is dependent on the pH of the medium and on the concentration of $H_4IO_6^-$ ion rather than on the total periodate concentration. The *cis*-cyclohexene glycol is more readily oxidized by periodic acid than is the *trans*-glycol. These data are interpreted on the basis of the formation of a cyclic intermediate ester between the periodate and the glycol as postulated by Criegee. Price and Knell picture this esterification to be a bimolecular inversion mechanism. The rate expression would be first order with respect to each of the reactants, whether the cyclic ester formation is the rate-determining step, or whether an equilibrium exists between the reactants and the cyclic ester and the decomposition of the ester is the rate-determining step. Duke[15] postulates the existence of an equilibrium forming a coordination complex intermediate between the glycol and periodate and that the disproportionation of this complex is the rate-determining step. This postulate is tested experimentally by measuring the rate of reaction between periodate and various excess amounts of glycol so that the free glycol concentration remains constant during any particular run. The observed results agree well with that expected from the postulate. By measuring the rate constant at two temperatures, the interesting observation is made that the energy of activation for the dis-



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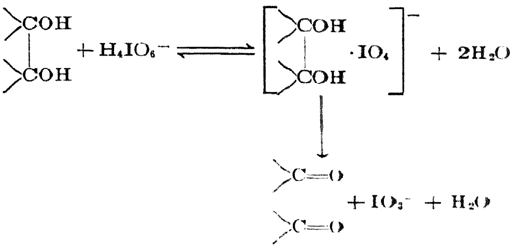
[13] C. C. Price and H. Kroll, *J. Am. Chem. Soc.*, **60**, 2726 (1938).

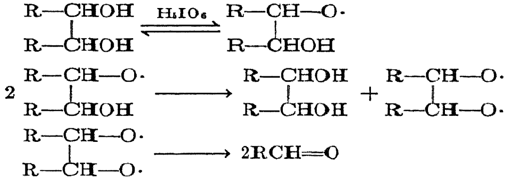
[14] C. C. Price and M. Knell, *ibid.*, **64**, 552 (1942).

[15] F. R. Duke, *J. Am. Chem. Soc.*, **69**, 3054 (1947).



proportionation of the complex is around 30 kcal. per mole, which is around 30 kcal. lower than the energy of the carbon-carbon single bond. This difference in energy is attributed to the formation of the complex and is held responsible for the specificity of the periodate as an oxididant for the α-diols.

Waters[16] contends that the cyclic ester formation is not necessary for the explanation of the Malaprade reaction. He postulates instead the removal of atomic hydrogen from the glycol ultimately to form a free diradical which is more readily stabilized by cleavage of the carbon-carbon bond than by eliminating the hydrogen atoms to form the diketone.



3. Properties of Periodic Acid and Periodates. Of the many hypothetical hydrates of iodine heptoxide which might be postulated only three are known to exist in reasonable amounts: paraperiodic acid, H_5IO_6; metaperiodic acid, HIO_4; and dimesoperiodic acid, $H_4I_2O_9$. The para acid is the only solid acid capable of existing in equilibrium with aqueous solutions. Heated at 80°C. in a vacuum, 2 moles of the para acid lose 3 moles of water forming the dimeso acid. Heated at 100° in a vacuum, the para acid loses 2 moles of water to form the meta acid. The anhydride of periodic acid, I_2O_7, has not been isolated.[17]

Paraperiodic acid forms colorless, monoclinic crystals which are hygroscopic and readily soluble in water and alcohol. The reagent can, therefore, be used conveniently as a standard, aqueous solution.

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[16] W. A. Waters, *Trans. Faraday Soc.*, 42, 184 (1946).

[17] J. R. Partington and R. K. Bahl, *J. Chem. Soc.*, 1934, 1088.

The properties of aqueous solutions of periodic acid were studied carefully by Crouthamel, Meek, Martin, and Banks.[18] They found that periodic acid behaves as a weak tribasic acid like phosphoric acid: it can be titrated sharply as a monobasic acid. The values for the three ionization constants which they reported are:

$$H_5IO_6 \rightleftharpoons H^+ + H_4IO_6^- \qquad K_1 = 2.30 \times 10^{-2}$$

$$H_4IO_6^- \rightleftharpoons H^+ + H_3IO_6^{2-} \qquad K_2 = 4.35 \times 10^{-9}$$

$$H_3IO_6^{2-} \rightleftharpoons H^+ + H_2IO_6^{3-} \qquad K_3 = 1.05 \times 10^{-15}$$

Periodic acid is a strong oxidizing agent which very slowly produces ozone from aqueous solutions. The titer of an aqueous solution thus changes gradually with time. Abel and Smetano[19] reported a value of 1.51 v. for the periodic acid-iodate couple. Because periodic acid quantitatively oxidizes manganous ion to permanganate in acid solution, Latimer[20] has pointed out that this value is too low; he gives for the couple:

$$H_5IO_6 + H^+ + 2e = IO_3^- + 3H_2O \qquad E^0 = \text{ca. } 1.7 \text{ v.}$$

Periodic acid forms salts which correspond to its stepwise neutralization by a base. Salts corresponding to the replacement of 1, 2, 3, and occasionally 5 equivalents of hydrogen ion by a metal are obtained, for example, $NaIO_4 \cdot 3H_2O$, $Na_2H_3IO_6$, $Na_3H_2IO_6$, and $Zn_5(IO_6)_2$. The periodate salts are generally only slightly soluble in water. The solubility is greater in hot water and is further increased by the addition of acids, especially of periodic or nitric acid. Potassium periodate is unique in this respect that its solubility is greater in basic than in acid solutions. At 25° the solubility of KIO_4 is 0.51 g. per 100 g. of water, whereas the solubility of $K_4I_2O_9$ is 14.0 g. per 100 g. of water.[21] Sodium metaperiodate is the most soluble of the salts of periodic acid which are readily available; at 25° its solubility is 14.5 g. per 100 g. of water. The high solubility makes sodium metaperiodate a very useful reagent for use in the Malaprade reaction. In addition, the solubility of sodium periodate is reduced greatly in basic solutions; the solubility of disodium paraperiodate is 0.23 g. per 100 g. of water. This simplifies the preparation of pure sodium periodate, and consequently it is used as the starting material for the preparation of other periodates and periodic acid.

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[18] C. E. Crouthamel, H. V. Meek, D. S. Martin, and C. V. Banks, *J. Am. Chem. Soc.*, **71**, 3031 (1949).

[19] E. Abel and O. Smetano, *Monatsh.*, **60**, 181 (1932).

[20] W. M. Latimer, *Oxidation Potentials*, Prentice-Hall, New York, 1938.

[21] A. E. Hill, *J. Am. Chem. Soc.*, **50**, 2678 (1928).

The preparation of periodic acid and periodates is described in detail elsewhere.[22] Fortunately, these compounds are available commercially so that it is not necessary to prepare them in the laboratory in order to use the Malaprade reaction.

4. Analytical Applications of the Malaprade Reaction. Periodate oxidations are generally carried out in aqueous solutions, but mixtures of water with methanol, ethanol, acetic acid, and dioxane have been used successfully as the solvent. The reacting substance need not be completely soluble; for example, starch and cellulose materials are readily oxidized in suspension. The reaction time for these heterogeneous systems is increased slightly to allow the reaction to proceed to completion.

The pH of the solution influences greatly the speed of the reaction. The optimum pH for the oxidation of polyhydroxy compounds is around 4. In strongly acidic or strongly basic solutions the reaction velocity is greatly decreased. The temperature of the reaction medium also influences the rate of reaction. At elevated temperatures the reaction velocity is increased greatly. The velocity of side reactions is also increased, so that these reactions interfere with the use of the Malaprade reaction. To keep these side reactions at a minimum, periodate oxidations are generally carried out at or below room temperature.

The oxidizing agent is usually prepared as a standard, aqueous solution of periodic acid, sodium metaperiodate, or potassium metaperiodate. These solutions are readily prepared from the commercially available reagents. With some samples a slight precipitate may form when the solution is prepared. The solution is then allowed to stand for at least 24 hours and filtered through a sintered-glass filter before standardizing and using for the oxidation of organic compounds. Sodium or potassium periodate is generally used when the acid produced by the Malaprade reaction is to be determined. These reagents are also generally used when the reaction is carried out in basic medium. A solution of paraperiodic acid or of the periodate salts and sulfuric acid is used when the reaction is carried out in acidic medium. Aqueous solutions of periodic acid and periodates are reasonably stable at room temperature but do decrease in titer with time. The solution should not be allowed to come in contact with oxidizable substances. The solutions are stored in glass bottles with glass stoppers.

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[22] *Inorganic Syntheses*, Vol. I, H. S. Booth, ed., McGraw-Hill, New York, 1939, pp. 168 ff.

Periodate solutions are readily standardized iodometrically by reduction of the periodate to iodate, in buffered, neutral to basic solutions.[23] These methods are described in greater detail on p. 273. In the presence of excess sodium bicarbonate, borax, or sodium phosphate as buffer, periodate is reduced to iodate by a slight excess of standard sodium arsenite solution containing a trace of iodide as catalyst. The excess arsenite is back-titrated with standard iodine solution. Potassium iodide, sodium thiosulfate, hydrogen peroxide, and manganous ion have been used as reducing agents in place of the arsenite. The presence of iodate does not interfere with the determination of periodate by these methods since the periodate is reduced only as far as the iodate state in neutral solution.

When the Malaprade reaction is used for the determination of polyhydroxy and amino alcohol type compounds, the analyses depend on the determination of (*a*) the periodate used in the oxidation and/or (*b*) the products of the Malaprade reaction.

The determination with periodate has the limitation that all substances which react with periodate are determined together and are not differentiated. This is, however, a very convenient method for determining the total number of equivalents of substances which react with periodate. A particular substance can be determined quickly and conveniently by this method if all other substances which react with periodate are known to be absent. For example, α-glycerophosphoric acid in a mixture of glycerophosphoric acids is readily determined by its reaction with periodic acid:[24]

$$\mathrm{CH_2OH{-}CHOH{-}CH_2{-}O{-}PO(OH)_2 + H_5IO_6 \longrightarrow HCHO + OHC{-}CH_2{-}O{-}PO(OH)_2 + HIO_3 + 3H_2O}$$

Several products of the Malaprade reaction have been determined to make the analysis more selective for certain types of organic compounds. The oxidations of carbonyl compounds and the polyhydroxy compounds, which can be considered as reacting with periodate via carbonyl compounds, result in the formation of carboxylic acids which can be determined by the acid-base titration. The determination of glycerol in the presence of glycols is a good example of the application of this method.

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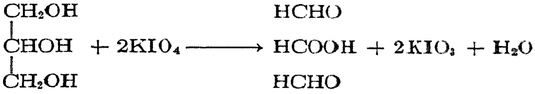
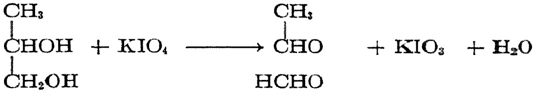
[23] E. Müller and G. Wegelin, *Z. anal. Chem.*, **52**, 755 (1913); J. Schwaibold, *ibid.*, **78**, 161 (1929); A. Schwicker, *ibid.*, **110**, 182 (1937); P. Fleury and J. Lange, *J. pharm. chim.*, (8) **17**, 107, 196 (1933); F. Rappaport, I. Reifer, and H. Weinmann, *Mikrochim. Acta*, **1**, 290 (1937); H. H. Willard and L. H. Greathouse, *J. Am. Chem. Soc.*, **60**, 2869 (1938); H. H. Willard and L. L. Merritt, Jr., *Ind. Eng. Chem., Anal. Ed.*, 14, 489 (1942); E. Kahane, *Bull. soc. chim. France*, **1948**, 70.

[24] P. Fleury and R. Paris, *Compt. rend.*, **196**, 1416 (1933); *J. pharm. chim.*, [8] **18**, 470 (1933); F. L. Pyman and H. A. Stevenson, *J. Chem. Soc.*, **1934**, 448.



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 2KIO_4 \longrightarrow \begin{array}{l} HCHO \\ HCOOH \\ HCHO \end{array} + 2KIO_3 + H_2O$$

glycerol



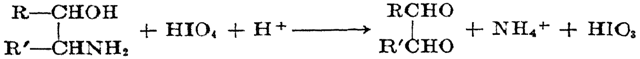
$$\begin{array}{l} CH_3 \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + KIO_4 \longrightarrow \begin{array}{l} CH_3 \\ | \\ CHO \\ HCHO \end{array} + KIO_3 + H_2O$$

propylene glycol

Each mole of glycerol yields one mole of formic acid, whereas the glycols yield only aldehydes.

The aldehyde formed by the periodate oxidation can be determined. The methods generally involve distillation or aeration of the aldehydes into a bisulfite solution and determination of the aldehyde iodometrically. The total number of equivalents of aldehyde can be determined in this way, or the aldehydes can be separated from one another and determined by fractional distillation or aeration. If the reaction medium contains amino acids and has a pH of 7, it is possible to aerate the higher aldehydes and not formaldehyde. For the example cited above, it is possible to determine in this way the amount of acetaldehyde formed by the periodate oxidation. This in turn makes possible the determination of propylene glycol in the presence of glycerol. After the higher aldehydes are volatilized, the formaldehyde remaining behind can be determined. In the example it can be seen that every primary alcohol or terminal amine group adjacent to an alcohol or carbonyl group is oxidized by periodate to formaldehyde. The determination of formaldehyde, therefore, gives a measure of the number of these groups and is useful in the study of the structure of carbohydrate and protein materials. Other methods like the gravimetric, polarographic, and spectrophotometric methods are also used for the determination of various aldehydes.

The amine group yields ammonium ions in the oxidation of α-amino alcohols.



$$\begin{matrix} \text{R—CHOH} \\ | \\ \text{R'—CHNH}_2 \end{matrix} + HIO_4 + H^+ \longrightarrow \begin{matrix} \text{RCHO} \\ | \\ \text{R'CHO} \end{matrix} + NH_4^+ + HIO_3$$

The amount of ammonia obtained from a basic solution of the periodate oxidation of a protein hydrolyzate can therefore be used to estimate the total hydroxyamino acid content of the sample.

DETERMINATION OF POLYHYDROXY COMPOUNDS

Glycerol: Each mole of glycerol when oxidized by periodate yields quantitatively 1 mole of formic acid. This distinguishes glycerol from the glycols and is the basis of the method for determining glycerol in the presence of glycols given by Allen, Charbonnier, and Coleman.[25]

Procedure: Transfer a sample containing enough glycerol and glycol to react with 2 millimoles of periodate (*ca.* 92 mg. of glycerol or 125 mg. of ethylene glycol) to a liter glass-stoppered Erlenmeyer flask and dilute to 50 ml. Add 50 ml. of approximately $0.05M$ periodic acid solution, mix, stopper, and allow to stand 40–80 minutes at room temperature. Add 100 ml. of water, mix, add exactly 2 drops of methyl red indicator, and titrate with standard $0.1N$ sodium hydroxide. Run a blank titration using 50 ml. of water in place of the sample. The difference in volume of sodium hydroxide used in the titration of the sample and the blank corresponds to the amount of acid produced by glycerol. One milliliter of $0.1N$ sodium hydroxide solution corresponds to 9.206 mg. of glycerol.

Notes: (1) The results obtained by Allen, Charbonnier, and Coleman show an average error of around 1 per cent. Part of this may be due to the complex solution which is titrated with sodium hydroxide. Among other substances, this solution contains excess periodic acid, iodic acid, and formic acid. The iodic acid, being a strong acid, does not cause difficulties. However, formic acid is a weak, monobasic acid having an ionization constant value of 1.77×10^{-4}, and periodic acid is a tribasic acid having ionization constant values of 2.30×10^{-2}, 4.35×10^{-9}, and 1.05×10^{-15}. For a titration carried out according to the procedure the formic acid concentration is approximately $3 \times 10^{-3}M$, and the periodic acid concentration approximately $10^{-3}M$. For such a solution, the equivalence point of the formic acid titration will have a pH of 7.6. The first equivalence point of the periodic acid will have a pH of 5.0. If the titration is stopped at pH 5, the formic acid titration end-point will not be reached and an error of -5.4 per cent will be introduced. In the other hand, if the titration is stopped at pH 7.6, part of the $H_4IO_6^-$ ions will be titrated to $H_3IO_6^{2-}$ and an error of $+5.0$ per cent will be introduced. Actually the methyl red end-point falls between these two extremes at approximately pH 6 so that the error is much less than 5 per cent. Nevertheless the end-point is less sharp than is the case for the titration of either periodic acid or formic acid separately.

(2) To correct for the obscure end-point, Bradford, Pohle, Gunther, and

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[25] N. Allen, H. Y. Charbonnier, and R. M. Coleman, *Ind. Eng. Chem., Anal. Ed.*, 12, 384 (1940).

Mehlenbacher[26] used a glass electrode pH meter and, using several small incremental additions of standard base solution near the end-point, titrated the complex mixture to an empirically determined end-point at pH 6.2. The blank was titrated to pH 5.4 and the true end-point and amount of glycerol were found by a complicated series of calculations.

Malaprade[27] outlined a procedure similar to those described above except that sodium metaperiodate was used as oxidant rather than periodic acid. The use of sodium metaperiodate is advantageous since the blank titer is thus greatly reduced. The concentration of excess periodate used in the oxidation was greater than that used in the above procedures and was reduced by adding potassium nitrate to the reaction mixture to precipitate potassium periodate before titrating with standard sodium hydroxide. By using solid potassium metaperiodate similar results are obtained. The periodate concentration in the solution treated by this procedure still is as great as or greater than that which remains by the method of Allen, Charbonnier, and Coleman. Methyl red is used as indicator in the titration of formic acid.

Khouvine and Arragon[28] prevent the excess periodate from interfering with the formic acid titration by the following method. A solution of barium hydroxide is added to the reaction mixture containing the excess periodate. The barium periodate is separated by centrifugation. The centrifugate solution is acidified with sulfuric acid and the formic acid is steam distilled. The distillate is titrated with standard hydroxide solution, phenolphthalein being used as indicator.

Halsall, Hirst, and Jones,[29] and Meyer and Rathgeb[30] used sodium andpotassium metaperiodate as oxidizing agents but freed the oxidation mixture of excess periodate by adding excess ethylene glycol before titrating with standard sodium hydroxide solution. Halsall, Hirst, and Jones used methyl red as indicator, but Meyer and Rathgeb used phenol red, which has a color change interval between pH 6.4 and 8.0. The transition interval of the latter indicator is nearer the equivalence point pH of the formic acid titration and thus increases the accuracy of the determination.

Since all organic compounds which can be considered to react with periodic acid through the α-dicarbonyl or α-carbonyl alcohol structure produce acids, the procedures which have been outlined above are used in determining these compounds in the presence of glycols. Therefore, although the discussion is in terms of the determination of glycerol, it is equally applicable to arabitol, mannitol, ketoses, and aldoses, disaccharides and polysaccharides having hydroxy groups on 3 or more adjacent carbon atoms. In fact, several of the methods described above were designed primarily for the study of carbohydrates and not for the determination of glycerol. On the other hand, it is possible to precipitate sugars from aqueous solutions with basic lead acetate,[31] leaving glycerol and glycols in solution so that glycerol in wines can be determined.

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[26] P. Bradford, W. D. Pohle, J. K. Gunther, and V. C. Mehlenbacher, *Oil & Soap*, **19**, 189 (1942).

[27] L. Malaprade, *Bull. soc. chim. France*, (5) **4**, 906 (1937).

[28] Y. Khouvine and G. Arragon, *Bull. soc. chim. France*, (5) **8**, 676 (1941).

[29] T. G. Halsall, E. L. Hirst, and J. K. N. Jones, *J. Chem. Soc.*, **1947**, 1399, 1427.

[30] K. H. Meyer and P. Rathgeb, *Helv. Chim. Acta*, **31**, 1540 (1948).

2,3-Butylene Glycol: The glycols upon oxidation with periodate yield only aldehydes and ketones. 2,3-Butylene glycol (2,3-butanediol) yields 2 moles of acetaldehyde per mole and thus can be distinguished from ethylene glycol, glycerol, arabitol, and other polyhydroxy compounds. By determining the amount of acetaldehyde produced by a periodate oxidation one obtains a measure of the 2,3-butylene glycol content of the sample. Other compounds having the $CH_3 \cdot CHOH—$ grouping attached to a carbon atom holding a hydroxyl or amine group, or attached to a carbonyl group will also produce acetaldehyde and be determined with the 2,3-butylene glycol. Thus, for example, 1,2-propylene glycol, methyl pentose, threonine, and acetoin each produces 1 mole of acetaldehyde per mole.

Birkenshaw, Charles, and Clutterbuck,[32] and Johnson[33] described procedures for the determination of 2,3-butylene glycol in fermentation products. The glycol is extracted with ether, transferred to the water layer by evaporating off the ether, and oxidized with periodic acid. The aldehyde produced is distilled into a solution of sodium bisulfite and determined iodometrically.

Procedure: Adjust the pH of the sample solution to a value greater than 7 to prevent the extraction of lactic acid. Extract the 2,3-butylene glycol from the solution with ether in a Soxhlet apparatus for 12 hours or more. Add water to the ether extract and evaporate off the ether. Transfer an aliquot portion of the solution containing 10 mg. or less of 2,3-butylene glycol to a 300 ml. Kjeldahl flask fitted with a dropping funnel and glass condenser. Dilute the sample to 50 ml. and add 5 ml. of N sulfuric acid and a pinch of talc to prevent bumping. The condenser outlet should dip into 10 ml. of approximately 1.25 per cent sodium bisulfite solution in a 250 ml. Erlenmeyer flask. Heat the sample until vapors reach the condenser and add 25 ml. of 0.01*M* potassium metaperiodate solution through the dropping funnel. Distill over the aldehyde produced for 5 minutes. The aldehyde is determined by oxidizing the excess bisulfite with 0.2*N* iodine solution. The solution is just decolorized with sodium thiosulfate solution. Add 10 ml. of saturated sodium bicarbonate solution to dissociate the aldehyde bisulfite compound and titrate the liberated bisulfite with standard 0.01*N* iodine solution to a starch end-point. Toward the end of the titration add 5 ml. of saturated bicarbonate and 1 ml. of 10 per cent sodium carbonate to ensure complete dissociation of the aldehyde-bisulfite compound. One milliliter of 0.01*N* iodine solution corresponds to 2.253 mg. of 2,3-butylene glycol.

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[31] G. Hoepe, *Helv. Chim. Acta*, **26**, 1931 (1943); E. Peynaud, *Ann. fals. fraudes* **41**, 384 (1948), *Chem. Abstr.*, **43**, 7635*i* (1949).

[32] J. H. Birkenshaw, J. H. V. Charles, and P. W. Clutterbuck, *Biochem. J.*, **25**, 1522 (1931).

[33] M. J. Johnson, *Ind. Eng. Chem., Anal. Ed.*, **16**, 626 (1944).

Notes: (1) Since the distillation of aldehyde is carried out from sulfuric acid solution, all aldehydes produced by the periodate oxidation are carried over. Fortunately, except for acetoin, substances which produce aldehydes are not present in the fermentation liquor or are not extracted by ether. If it should be necessary, procedures for separating the various aldehydes may be adopted.

(2) The determination of aldehyde is made essentially by the method described by Clausen,[34] Donnally,[35] Friedemann, Cotonio, and Shaffer,[36] and Jaulmes and Espezel.[37] These authors point out that the aldehyde is best absorbed in neutral or slightly basic bisulfite solution. They also point out the importance of oxidizing the excess bisulfite in acid solution to avoid the possible dissociation of the aldehyde bisulfite compound.

Brockmann and Werkman[38] describe a modification of the above procedure for the determination of 2,3-butylene glycol in fermentations. The glycol is steam-distilled from a solution of the sample made alkaline with sodium carbonate. The glycol is oxidized with potassium metaperiodate in sulfuric acid solution and the aldehyde produced by the reaction aerated into standard hydroxylamine hydrochloride solution. The aldehyde is determined by neutralizing the hydroxylamine solution with 0.1*N* sodium hydroxide to the methyl orange end-point, adding neutral acetone, and titrating the liberated acid with standard hydroxide. The difference between the sample and blank titers gives the amount of aldehyde present.

Methylpentose in Presence of Pentose: Nicolet and Shinn[39] found that acetaldehyde is quantitatively aerated from a solution having pH near 7, preferably between pH 7.0 and 7.2, whereas formaldehyde is held in the solution if it contains sufficient amino acid. The acetaldehyde is collected in a solution of bisulfite and determined iodometrically. Methylpentose is determined readily by this method in the presence of pentose.

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[34] S. W. Clausen, *J. Biol. Chem.*, 52, 263 (1922).

[35] L. H. Donnally, *Ind. Eng. Chem., Anal. Ed.*, 5, 91 (1933).

[36] T. E. Friedemann, M. Cotonio, and P. A. Shaffer, *J. Biol. Chem.*, 73, 335 (1927).

[37] P. Jaulmes and R. Espezel, *Ann. fals. et fraudes*, 28, 325 (1935); *Chem. Abstr.*, 29, 7008 (1935).

[38] M. C. Brockmann and C. H. Werkman, *Ind. Eng. Chem., Anal. Ed.*, 5, 206 (1933).

[39] B. H. Nicolet and L. A. Shinn, *J. Am. Chem. Soc.*, 63, 1456 (1941).

Procedure: Three 25 × 200 mm. Pyrex test tubes are connected as a gas absorption train except that the first test tube which is the reaction tube also has a dropping funnel with its tube almost to the bottom of the test tube. The periodic acid solution and the carbon dioxide for aeration are introduced through the dropping funnel.

Transfer to the reaction tube an aliquot portion (not exceeding 5 ml.) of sample solution containing 5–15 mg. of methylpentose. Add 0.2 g. of alanine to retain the formaldehyde, 1 drop of Nujol to prevent foaming, 5 ml. of $1M$ sodium bicarbonate, and 10 ml. of $0.1N$ sodium arsenite. Add 5 ml. of 2 per cent sodium bisulfite solution to the second tube; 3 ml., to the third; and dilute both to a volume of 25 ml. Pass carbon dioxide through the system for a few seconds to mix the solutions. Add 2 ml. of $0.5M$ periodic acid solution to the reaction tube and pass carbon dioxide for 1 hour at a rate of about 1 liter per minute.

Transfer the contents of the second and third test tubes quantitatively to a titration flask and determine the acetaldehyde content iodometrically as follows.[40] Destroy the excess bisulfite with $0.1N$ iodine solution. Carefully adjust the end-point of the titration to the blue starch-iodine color with $0.02N$ iodine solution. Add sufficient saturated sodium bicarbonate solution to discharge the blue color and titrate the bisulfite liberated from the acetaldehyde-bisulfite compound with standard $0.02N$ iodine solution. Each ml. of standard $0.02N$ iodine solution is equivalent to 1.64 mg. of methylpentose.

Glycerol, Ethylene Glycol, and 1,2-Propylene Glycol: By determining the periodate consumed and some of the products of the Malaprade reaction, it is possible to determine several polyhydroxy compounds in the presence of one another. Shupe[41] applied this scheme to the determination of glycerol, ethylene glycol, and 1,2-propylene glycol in the fats and waxes used in cosmetic materials. These substances react with potassium periodate according to the equations:

$$\mathrm{CH_2OH{-}CHOH{-}CH_2OH + 2KIO_4 \longrightarrow 2HCHO + HCOOH + 2KIO_3 + H_2O}$$

$$\mathrm{CH_2OH{-}CH_2OH + KIO_4 \longrightarrow 2HCHO + KIO_3 + H_2O}$$

$$\mathrm{CH_3{-}CHOH{-}CH_2OH + KIO_4 \longrightarrow CH_3CHO + HCHO + KIO_3 + H_2O}$$

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[40] S. W. Clausen, *J. Biol. Chem.*, 52, 263 (1922); H. C. Troy and P. F. Sharp, *Cornell Univ. Agr. Expt. Sta. Mem., No.* 179 (1935).

[41] I. S. Shupe, *J. Assoc. Offic. Agr. Chemists*, 26, 249 (1943).

Glycerol yields formic acid, which is titrated with standard base; 1,2-propylene glycol yields acetaldehyde, which is separated from formaldehyde and determined by the bisulfite method; and ethylene glycol is determined by difference from the total aldehyde produced or from the periodate consumed.

Procedure: Dissolve the sample in water and make neutral to methyl red. Transfer to a 100 ml. volumetric flask an aliquot portion of sample containing not more than 2 meq. of oxidizable substance, i.e., 45 mg. of glycerol or its equivalent. Add 50 ml. of $0.02M$ potassium periodate, dilute the solution to the volume mark with water, and allow to stand at room temperature for 1 hour. Make the following determinations on aliquot portions of this oxidized mixture:

(*a*) *Glycerol* (*Formic Acid*): To a 20 ml. aliquot portion, add 1 drop of methyl red indicator solution and titrate with $0.02N$ standard sodium hydroxide to a yellow color. Run a blank titration. The difference in volume of sodium hydroxide solution used to titrate the sample and blank (designated as A ml.) corresponds to the amount of formic acid produced. One milliliter of $0.02N$ sodium hydroxide corresponds to 0.921 mg. of formic acid or to 1.841 mg. of glycerol.

(*b*) *Excess Periodate:* Dilute the solution titrated for formic acid to approximately 50 ml., add approximately 0.5 g. of sodium bicarbonate, and stir thoroughly. Add 0.2 g. of potassium iodide and 5 ml. of 0.5 per cent starch solution. Titrate the liberated iodine with $0.02N$ standard arsenite solution to the disappearance of the blue color. Allow about 5 minutes for the reaction to reach equilibrium before establishing the final end-point. Titrate the blank to standardize the periodate solution. The difference in titer for the sample and blank (designated as B ml.) corresponds to the amount of periodate consumed in the oxidation.

(*c*) *1,2-Propylene Glycol* (*Acetaldehyde*): Set up a gas absorption train using four 150 × 25 mm. test tubes in series. Pipette a 20 ml. aliquot portion of the oxidized mixture to the first test tube and add approximately 2 g. of sodium bicarbonate. To the second test tube add approximately 0.2 g. of glycine, 1 g. of sodium bicarbonate, and 10 ml. of water. To each of the third and fourth tubes add 1 ml. of 5 per cent sodium bisulfite and 15 ml. of water; the exact concentration and amount of bisulfite need not be known. Pass a stream of carbon dioxide through the train for 1 hour at the rate of approximately 1.5 liters per minute. The slightly basic glycine solution absorbs formaldehyde and allows the higher aldehydes to pass on to be absorbed in the sodium bisulfite solutions in the third and fourth tubes. Transfer quantitatively the solutions in these last two tubes to a titration flask; the total volume of solution including washings should be about 50 ml. Add starch, and $0.5N$ iodine solution until the first permanent blue color appears.

Add a drop of sodium bisulfite solution to decolorize the solution and adjust to the starch end-point with $0.02N$ iodine solution. Add 10 ml. of solution containing 0.4 g. of borax and 0.5 g. of sodium carbonate to destroy the acetaldehyde-bisulfite compound and titrate the liberated bisulfite with standard $0.02N$ iodine solution. The amount of iodine solution used in this final titration (designated as C ml.) corresponds to the amount of acetaldehyde present in the solution. One milliliter of $0.02N$ iodine solution corresponds to 0.440 mg. of acetaldehyde or 0.760 mg. of 1,2-propylene glycol.

(*d*) *Total Aldehydes:* Pipette a 20 ml. aliquot portion of the oxidized mixture into 5 ml. of 5 per cent sodium bisulfite solution in a titration flask and allow to stand for 30 minutes. Dilute to 50 ml. and determine the aldehydes by the procedure outlined above for the determination of acetaldehyde in the third and fourth test tubes. Let the volume of standard iodine solution required in the final titration be designated by D ml.

(*e*) *Calculations:* The weight of glycerol in the sample is calculated from the titration in (*a*):

$$\text{wt. of glycerol} = A \times 1.842 \times 5 = 9.210 \times A \text{ mg.}$$

The weight of 1,2-propylene glycol in the sample is calculated from the titration in (*c*):

$$\text{wt. of 1,2-propylene glycol} = C \times 0.760 \times 5 = 3.800 \times C \text{ mg.}$$

The weight of ethylene glycol in the sample is calculated from the titration in (*b*) or (*d*) after correcting for the glycerol and propylene glycol:

$$\text{wt. of ethylene glycol} = 3.100\ (B - 4A - C) \text{ mg.} = 1.550\ (D - 4A - 2C) \text{ mg.}$$

Notes: (1) The determination of formic acid in (*a*) can be improved by removing the excess periodate before titrating with sodium hydroxide (see p. 487).

(2) In buffered, netural solution, periodate is reduced to iodate by iodide; thus the equivalent weight of periodate is one half the molecular weight.

(3) When a solution containing aldehydes and some amino acids is buffered at a pH near 7, preferably between pH 7.0 and 7.2, and bubbled with carbon dioxide, formaldehyde is held by the amino acid while the higher aldehydes are volatilized. Thus the second test tube in (*c*) retains formaldehyde but allows acetaldehyde to be carried to the third and fourth tubes. The method of analysis is essentially that developed by Nicolet and Shinn for determining methylpentose in the presence of pentose which is described above.

Reinke and Luce[42] described a method for determining 1,2-propylene glycol and ethylene glycol in the presence of one another which is a slight modification of the method of Shupe. The total glycol is calculated from the amount of periodate consumed in the oxidation, and the 1,2-propylene glycol from the amount of acetaldehyde formed. The ethylene glycol is calculated by difference.

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[42] R. C. Reinke and E. N. Luce, *Ind. Eng. Chem., Anal. Ed.*, 18, 244 (1946).

Hoepe and Treadwell[43] used a different method for determining glycerol, ethylene glycol, and 1,2-propylene glycol. Since only glycerol yields formic acid when oxidized by periodate, it is determined by titration with standard base solution. Total aldehyde produced is determined by the acidimetric-bisulfite method. The reaction of aldehyde with sodium sulfite may be written:

$$\text{RCHO} + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{RCH(OH)(SO}_3\text{Na)} + \text{NaOH}$$

The free sodium hydroxide is titrated with standard acid solution. Formaldehyde is determined in the presence of acetaldehyde by the cyanide method (see p. 304). According to Hoepe and Treadwell the reaction product is the addition compound of hydrocyanic acid to the aldehyde and not glycolate, as has been claimed in the literature. The cyanide used in the formation of the addition compound is determined argentometrically.

Procedure: Add 0.4–0.5 g. of sample to a 100 ml. glass stoppered bottle, mix with 50 ml. of water and 2.5–3.0 g. of solid potassium metaperiodate. Shake the mixture mechanically for 2 hours. Filter off the excess potassium periodate, collecting the filtrate and washings in a 100 ml. volumetric flask. Dilute the solution to the volume mark.

(*a*) *Glycerol* (*Formic Acid*): Transfer a 20 ml. aliquot sample of the oxidized solution to a titration flask, add methyl red as indicator, and titrate with standard 0.1*N* sodium hydroxide solution. Each milliliter of 0.1*N* sodium hydroxide corresponds to 9.20 mg. of glycerol.

(*b*) *Total Aldehydes:* Transfer a 25 ml. aliquot sample of the oxidized solution to a titration flask, add 50 ml. of 12.5 per cent sodium sulfite solution, thymolphthalein as indicator, and titrate with standard 0.1*N* hydrochloric acid solution. Run a blank to determine the alkalinity of the sodium sulfite solution. Each milliliter of 0.1*N* hydrochloric acid corresponds to 0.1 millimole of aldehyde.

(*c*) *Formaldehyde:* Take a 25 ml. aliquot sample of the oxidized solution, add 0.5 ml. of 50 per cent nitric acid and 30 ml. of standard 0.1*N* silver nitrate solution. Filter off the precipitate of silver iodate and silver periodate, washing the precipitate with a little, very dilute nitric acid. Titrate the excess silver in the filtrate by the Volhard method. Take another 25 ml. aliquot of the oxidized solution, add 30 ml. of standard 0.1*N* potassium cyanide solution and exactly the same amounts of nitric acid and silver nitrate as added above. Filter off the precipitate of silver iodate, periodate, and cyanide. Wash the precipitates with the very dilute nitric acid and titrate the filtrate as before by the Volhard method. The difference in volume of standard 0.1*N* ammonium thiocyanate used in these two Volhard titrations corresponds to the amount of "free" cyanide. The cyanide combined with formaldehyde corresponds to the 30 ml. added less the volume equivalent to "free cyanide." Each milliliter of cyanide combined corresponds to 0.1 millimole of formaldehyde.

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[43] G. Hoepe and W. D. Treadwell, *Helv. Chim. Acta*, 25, 353 (1942).

(*d*) *Calculations:*

$$\text{wt. of glycerol in sample} = 0.04602\ (\text{ml. } 0.1N\ \text{NaOH})\ \text{g.}$$

$$\text{wt. of 1,2-propylene glycol in sample} = 0.3042\ ((\text{millimoles aldehyde}) - (\text{millimoles formaldehyde}))\ \text{g.}$$

$$\text{wt. of ethylene glycol in sample} = 0.1241\ (2(\text{millimoles formaldehyde}) - (\text{millimoles aldehyde}) - 0.25\ (\text{ml. } 0.1\ N\ \text{NaOH}))\ \text{g.}$$

Glycerol and 2,3-Butylene Glycol in Presence of Sugars: Sugars present in solutions with glycerol and glycols are oxidized by periodates to yield aldehydes and acids. Sugars must, therefore, be removed if the glycerol and glycols are to be determined by the periodate method.

Hoepe[44] precipitated sugars from wines with basic lead acetate, steam-distilled the glycerol and butylene glycol from the filtrate; then used the method of Hoepe and Treadwell described above for the determination of glycerol and glycol.

Peynaud[45] described a method for determining glycerol and 2,3-butylene glycol in wine. The sugars are removed with lead hydroxyacetate and calcium hydroxide in ethanol solution before the glycerol is determined by periodate oxidation.

Diglycols and Monoglycols in Presence of One Another: Diglycols, like diethylene glycol or dipropylene glycol, are not oxidized by periodic acid but they are oxidized by dichromate. Therefore, in a mixture of monoglycol and diglycol it is possible to destroy and determine the monoglycol with periodic acid, distill out the aldehydes produced, and determine the diglycol by oxidation with potassium dichromate. Another method of determining the diglycol is to determine the monoglycol in an aliquot portion of the sample with periodic acid. A second aliquot portion can then be treated with potassium dichromate. The dichromate necessary to oxidize the monoglycol is subtracted from the dichromate necessary for the sample to obtain that necessary to oxidize the diglycol.

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[44] G. Hoepe, *Helv. Chim. Acta*, **26**, 1931 (1943).

[45] E. Peynaud, *Ann. fals. et fraudes*, **41**, 384 (1948); *Chem. Abstr.*, **43**, 7635*i* (1949).

The first method was described by Francis.[46] Although he used the polarographic method to determine the excess dichromate, an iodometric method could be used.

Diethylene glycol should be oxidized by dichromate according to the equation:

$$3CH_2OH—CH_2—O—CH_2—CH_2OH + 10K_2Cr_2O_7 + 40H_2SO_4 \longrightarrow 12CO_2 + 10Cr_2(SO_4)_3 + 10K_2SO_4 + 55H_2O$$

Accordingly, the number of grams of diethylene glycol oxidized per gram of potassium dichromate would be 0.1082. Empirically this factor is found to have the value 0.1381. Although there is no explanation for the discrepancy, the empirical factor is reproducible and thus the method can be used.

Another method is described by Allen, Charbonnier, and Coleman.[47] The original papers should be consulted for details.

Determination of Structure in Complex Polyhydroxy Compounds: The Malaprade reaction is a great asset in the study of the structure of complex compounds like sugars, starches, dextrins, and polymers. This application of the Malaprade reaction has been discussed in recent reviews.[48] Since the determination of structure is of more interest from the organic than from the analytical point of view, little mention need be made of it here. It will suffice to say that the periodate method has provided some useful information on polymerization studies.[49]

Jackson and Hudson[50] oxidized corn starch and cotton cellulose with periodic acid and hydrolyzed the product in dilute hydrochloric acid. They identified as products glyoxal and *d*-erythrose which indicates cleavage of the hexose unit in starch and cellulose between the second and third carbon atoms. This confirms the generally accepted structure of the predominating unit in polysaccharides. The terminal units yield, on oxidation, formic acid and formaldehyde. Caldwell and Hixon[51] determined the amount of formaldehyde produced as a measure of the number of terminal groups in starch and consequently the number of hexose units in a starch molecule. More recently this method has been applied to a study of structure in carbohydrates by Barry, Meyer and Rathgeb, Halsall, Hirst, and Jones, and Bell, among others.[52]

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[46] C. V. Francis, *Anal. Chem.*, **21**, 1238 (1949).

[47] N. Allen, H. Y. Charbonnier, and R. M. Coleman, *Ind. Eng. Chem., Anal. Ed.*, **12**, 384 (1940).

[48] L. N. Owen, *Ann. Repts. on Progr. Chem. (Chem. Soc. London)*, **40**, 115 (1943); E. L. Jackson, in *Organic Reactions*, Vol. II, Chapt. 8, R. Adams *et al.*, ed., Wiley, New York, 1944.

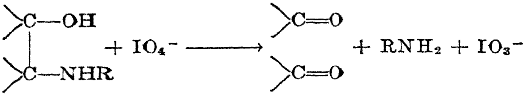
[49] C. S. Marvel and C. E. Denoon, Jr., *J. Am. Chem. Soc.*, **60**, 1045 (1938); P. J. Flory and F. S. Leutner, *J. Polymer Sci.*, **3**, 880 (1948).

[50] E. L. Jackson and C. S. Hudson, *J. Am. Chem. Soc.*, **60**, 989 (1938).

[51] C. G. Caldwell and R. M. Hixon, *J. Biol. Chem.*, **123**, 595 (1938).

DETERMINATION OF HYDROXYAMINO COMPOUNDS

Hydroxyamino compounds having the hydroxy and amino groups on adjacent carbon atoms are oxidized quickly and quantitatively by periodate at room temperature in weakly basic aqueous medium. The reaction proceeds according to the general equation:



$$\begin{array}{l} >C-OH \\ \quad | \\ >C-NHR \end{array} + IO_4^- \longrightarrow \begin{array}{l} >C=O \\ \\ >C=O \end{array} + RNH_2 + IO_3^-$$

where R can be a hydrogen atom or a substituent other than an acyl group. The organic compound is oxidized to two carbonyl compounds and an amine or ammonia; the periodate is reduced to iodate. Analytical application of the periodate oxidation depends on the determination of the periodate reduced, the amine or ammonia produced, or the aldehydes formed. Analytical studies have been devoted almost exclusively to the α-hydroxyamino compounds in protein materials, but the results and methods derived may be applied to the determination of α-hydroxyamino compounds in other materials and mixtures.

Total α-Hydroxyamino Content: α-Hydroxyamino compounds having primary amino groups when oxidized by periodate yield 1 mole of ammonia per mole. The determination of these compounds thus involves simply the determination of ammonia produced by their reaction with periodate. For further discussion on the determination of ammonia, see Vol. II, pp. 168–176.

Van Slyke and his coworkers[53] treated samples of amino acids with periodate and potassium carbonate, aerated the liberated ammonia into a solution of sulfuric acid, and determined the ammonia either acidimetrically or manometrically. Of the amino acids found in proteins, the only compounds found to have an α-hydroxyamino structure are hydroxylysine, serine, threonine, and β-hydroxyglutamic acid. No amino acid without the α-hydroxyamino group has been found to yield ammonia under the conditions of the analysis. Tryptophan, methionine, and cystine react rapidly with periodate but do not produce ammonia. Glycine, alanine, tyrosine, histidine, aspartic acid, asparagine, and glutamic acid react very slowly with periodate but do not produce ammonia under the conditions of the analysis. Ammonia originally present in the sample solution can be volatilized from basic solution before the periodate is added. Carbohydrates and other polyhydroxy compounds which react with periodate do not interfere.

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[52] V. C. Barry, *Nature*, **152**, 538 (1943); K. H. Meyer and P. Rathgeb., *Helv. Chim. Acta*, **31**, 1548 (1948); T. G. Halsall, E. L. Hirst, and J. K. N. Jones, *J. Chem. Soc.*, **1947**, 1399, 1427; F. Brown, T. G. Halsall, E. L. Hirst, and J. K. N. Jones, *ibid.*, **1948**, 27; D. J. Bell, *J. Chem. Soc.*, **1948**, 992.

[53] D. D. Van Slyke, A. Hiller, D. A. MacFadyen, A. B. Hastings, and F. W. Klemperer, *J. Biol. Chem.*, **133**, 287 (1940); D. D. Van Slyke, A. Hiller, and D. A. MacFadyen, *ibid.*, **141**, 681 (1941).

Procedure: If the sample is a protein, hydrolyze a portion by refluxing with 6*M* hydrochloric acid solution for at least 24 hours. The excess acid is then removed by evaporating the solution *in vacuo*.

Determine the ammonia produced by periodate oxidation, and therefore the hydroxyamino acid in the protein, using a Van Slyke-Cullen gas aeration apparatus.[54] To the receiving tube add 15 ml. of 2 per cent boric acid or 15 ml. of 0.02*N* standard hydrochloric or sulfuric acid solution. To the generation tube add, in order: a 5 ml. aliquot of protein hydrolyzate containing hydroxyamino acid to yield 0.1–2 mg. of ammonia nitrogen, 1 ml. of 5 per cent glycine, 1 drop of caprylic alcohol, 1 ml. of 2 *N* sodium hydroxide, 10 ml. of saturated potassium carbonate, and 2 ml. of 0.2*M* periodic acid. Since ammonia is liberated when the periodic acid is added, close the system after its addition before ammonia escapes. Pass air through the system slowly at first (about one bubble per second for 2 minutes). Gradually increase aeration to 4 liters per minute at the end of 5 minutes. Draw air through the system for 25 minutes so that 100 liters is passed. Determine the ammonia acidimetrically: if boric acid is used in the receiving tube, titrate the ammonia with standard 0.02*N* acid with bromcresol green as indicator; if hydrochloric or sulfuric acid is used, titrate the excess acid with standard 0.02*N* base with alizarin red as indicator. Each milliliter of standard 0.02*N* acid solution is equivalent to 0.02 millimole of hydroxyamino acid or 2.10 mg. calculated as serine.

Notes: (1) Either boric acid or a strong acid solution may be used to absorb the volatilized ammonia; the boric acid method is used when less than 1.5 mg. of ammonia nitrogen is involved, and the strong acid method when more than 1.5 mg. of ammonia nitrogen is involved.

(2) The ammonia can be determined manometrically. If this method is used, the ammonia is first aerated into 12 ml. of 0.1*N* sulfuric acid.

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[54] D. D. Van Slyke and G. E. Cullen, *J. Biol. Chem.*, 19, 211 (1914); 24, 117 (1916).

(3) If the protein hydrolyzate sample contains ammonia this can be determined first by carrying out the procedure, omitting the periodic acid. After the free ammonia is determined, add a fresh acid solution to the receiving tube and the 2 ml. of 0.2*M* periodic acid to the reaction tube and determine the hydroxyamino nitrogen as above.

Martin and Synge[55] used a very similar procedure but a generation-absorption apparatus similar to that used by Friedemann, Cotonio, and Shaffer.[56]

Nicolet and Shinn[57] used essentially the same principle for analysis but simplified the apparatus and procedure. Their apparatus consists of two pairs of 25 x 200 mm. Pyrex test tubes connected in series as a gas train. The first tube of one pair is fitted with a separatory funnel the stem of which reaches nearly to the bottom of the test tube and serves to introduce periodic acid and air into the system.

Gordon, Martin, and Synge[58] reported another modification of this analysis using a Conway diffusion unit (p. 31).

Hydroxylysine in Proteins: Hydroxylysine is separated from serine, threonine, β-hydroxyglutamic acid, and other monoamino acids by precipitation with phosphotungstic acid. The phosphotungstates of the diamino acids are much less soluble than those of the monoamino acids in 0.25*M* hydrochloric acid.[59]

Macpherson[60] used electrodialysis to separate the basic amino acids. Under the action of direct current the basic amino acids migrate to the cathode chamber.

Threonine in Protein: The reaction of threonine (α-amino-β-hydroxybutyric acid) with periodate is represented by the equation

$$\mathrm{CH_3{-}CHOH{-}CH(NH_2){-}COOH + IO_4^- \longrightarrow CH_3CHO + OHC{-}COOH + NH_3 + IO_3^-}$$

Of the amino acids generally present in protein materials, threonine is the only one which has been found to form acetaldehyde when treated with periodate. Acetaldehyde is readily determined in the presence of formaldehyde and nonvolatile aldehydes (see determination of 2,3-butylene glycol, methylpentose, 1,2-propylene glycol, pp. 488–494), and therefore the threonine content of proteins is readily determined.

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[55] A. J. P. Martin and R. L. M. Synge, *Biochem. J.*, **35**, 294 (1941).

[56] T. E. Friedemann, M. Cotonio, and P. A. Shaffer, *J. Biol. Chem.*, **73**, 335 (1927).

[57] B. H. Nicolet and L. A. Shinn, *J. Biol. Chem.*, **142**, 139 (1942).

[58] A. H. Gordon, A. J. P. Martin, and R. L. M. Synge, *Biochem. J.*, **37**, 538 (1943).

[59] D. D. Van Slyke, A. Hiller, and D. A. MacFadyen, *J. Biol. Chem.*, **141**, 681 (1941); D. D. Van Slyke, *J. Biol. Chem.*, **10**, 15 (1911–12); **22**, 281 (1915).

[60] H. T. Macpherson, *Biochem. J.*, **40**, 470 (1946).

Martin and Synge, and Shinn and Nicolet,[61] oxidized protein hydrolyzate with periodate at room temperature in a solution containing an excess of sodium bicarbonate. The acetaldehyde is aerated from this solution into a solution of sodium bisulfite, whereas formaldehyde remains behind. The acetaldehyde absorbed by the bisulfite is then determined iodometrically.

Winnick[62] modified the method of Shinn and Nicolet described above by substituting the Conway micro diffusion apparatus for the aeration apparatus. He also used different buffer solutions but the principle of the analysis is the same. The advantage of the micro diffusion method is the simplicity of the apparatus and its ease of operation.

Serine in Proteins: The reaction of serine, α-amino-β-hydroxypropionic acid, with periodate represented by the equation:

$$CH_2OH\text{—}CH(NH_2)\text{—}COOH + IO_4^- \longrightarrow HCHO + OHC\text{—}COOH + NH_3 + IO_3^-$$

gives rise to formaldehyde and glyoxylic acid. In contradistinction to the polyhydroxy compounds which commonly yield formaldehyde on oxidation with periodate, among the naturally occurring amino acids only serine and hydroxylysine have been observed to yield formaldehyde. The determination of formaldehyde formed by periodate oxidation, therefore, serves as a determination of serine and hydroxylysine in proteins. As pointed out above (p. 498) the diamino acid, hydroxylysine, can be separated from the monoamino acids by precipitation as the phosphotungstate. This makes possible the determination of serine in proteins by the determination of formaldehyde.

Formaldehyde in periodate oxidation mixtures is determined best by volatilizing acetaldehyde and low-boiling, higher homologues from solution buffered around pH 7 and containing some amino acids, followed by the isolation of formaldehyde: (1) as the 5,5-dimethylcyclohexane-1,3-dione (dimethyldihydroresorcinol, *dimedon* or methon) derivative, (2) by volatilization from the acidified solution, or (3) colorimetrically as the chromotropic acid derivative.

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[61] A. J. P. Martin and R. L. M. Synge, *Nature*, **146**, 491 (1940); *Biochem. J.*, **35**, 294 (1941); L. A. Shinn and B. H. Nicolet, *J. Biol. Chem.*, **138**, 91 (1941).

[62] T. Winnick, *J. Biol. Chem.*, **142**, 461 (1942).

Nicolet and Shinn, and Martin and Synge,[63] utilized the dimedon derivative for the isolation of formaldehyde and the determination of serine.

Rees[64] steam-distilled formaldehyde from an acid solution after the acetaldehyde was removed. The formaldehyde was collected in sodium bisulfite solution and determined iodometrically.

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[63] B. H. Nicolet and L. A. Shinn, *J. Biol. Chem.*, **139**, 687 (1941); A. J. P. Martin and R. L. M. Synge, *Biochem. J.*, **35**, 294 (1941).

[64] M. W. Rees, *Biochem. J.*, **40**, 632 (1946).

TITRATIONS

CHAPTER XII

POTASSIUM BROMATE AS A TITRIMETRIC REAGENT

1. General Considerations. In acid solution bromate is a strong oxidant; bromide is formed in the first stage of the reaction and then reacts with excess of bromate to yield free bromine

$$BrO_3^- + 6H^+ + 6e \longrightarrow Br^- + 3H_2O$$

$$BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br_2 + 2H_2O$$

It is usual to add bromide to the test solution before the titration or to include it in the standard bromate solution so that only the second reaction is involved.

An acidified mixture of bromate and bromide actually behaves as an equivalent solution of bromine. Thus the stable bromate-bromide solution serves for the extemporaneous preparation of a standard solution of bromine. Aqueous bromine solutions are unstable because of the high vapor pressure of bromine. Nevertheless, several authors have suggested the use of standard bromine solutions in aqueous or nonaqueous solvents; a brief account of their work is given on p. 564. Acidified solutions of bromate-bromide have been used extensively for the determination of inorganic and organic substances (p. 506), of organic aromatic compounds by substitution reactions (p. 534), and for the determination of unsaturation by addition reactions (p. 569).

When the reaction between the reducing compound and bromine in acid solution is very rapid, a direct titration can be carried out and the end-point may be detected by the appearance of the bromine color or by a reversible or irreversible indicator (p. 502). The indicator error becomes appreciable in very dilute solutions. In such cases, a simple amperometric titration with one or two platinum indicator electrodes becomes ideally suitable.[1]

When the reaction between bromine and the substance to be determined is not instantaneous, an excess of reagent is added and the excess of bromine determined iodometrically or with arsenious trioxide. Because bromine is so volatile, losses by evaporation must be avoided. Several authors have recommended special titration cells for this purpose,[2] but it is more customary to use an iodine flask or a specially designed bromine flask; these are described on p. 29.

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[1] For details, see I. M. Kolthoff and J. J. Lingane, *Polarography*, Vol. II, Interscience, New York-London, 1952.

The oxidizing action of bromate appears to have been noted by Balard[3] during his work on the existence of bromine in sea water, but the first application of bromate as a titrimetric reagent was due to Koppeschaar,[4] who used it in his now well-known bromination procedure for the determination of phenol (see p. 537). Kratschmer[5] first recommended the use of bromate as an oxidimetric reagent. Feit and Kubierschky,[6] who carried out an extended study, made special mention of the high stability of standard bromate solutions. Györy[7] avoided the iodometric back-titration by titrating directly with potassium bromate, in the presence of methyl orange as indicator, the latter being bleached at the end-point. He determined arsenic(III) and antimony(III) in this way. Györy's method has found wide application and has been subjected to only minor changes since his day.

Smith[8] proposed that a mercuric salt be added so that when weak reducing substances are titrated, the reduction stage is not stayed at the formation of free bromine, but proceeds further to bromide, owing to the formation of undissociated mercuric bromide.[9] He recommended that ferrous iron, chromium(III), and certain other substances should be titrated thus.

Detection of the End-Point: It has already been stated that Györy used methyl orange as indicator in direct titrations with potassium bromate (cf. p. 506); the dyestuff is irreversibly bleached at the end-point. Several other dyestuffs have been recommended, e.g., indigo carmine and methyl red.

Smith and Bliss[10] tested a large number of dyestuffs as indicators for bromate titrations. Those finally recommended are included in Table I; they are said to be preferable to the earlier irreversible indicators. Smith and May[11] later added bordeaux to this list. It may be noted, however, that they were under the mistaken impression that an elevated temperature was necessary for titrations done with methyl orange as indicator. Györy certainly does not specify this condition, and the heating of the solution appears to have been first proposed by Nissenson and Siedler.[12]

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[2] See, e.g., J. D'Ans and P. Höfer, *Z. angew. Chem.*, **47**, 71 (1934).

[3] Balard, *Ann. chim. et phys.*, (2) **32**, 337 (1826).

[4] W. F. Koppeschaar, *Z. anal. Chem.*, **15**, 233 (1876).

[5] Kratschmer, *Z anal. Chem.*, **24**, 546 (1885).

[6] W. Feit and K. Kubierschky, *Chem. Ztg.*, **15**, 350 (1891).

[7] S. Györy, *Z. anal. Chem.*, **32**, 415 (1893).

[8] G. F. Smith, *J. Am. Chem. Soc.*, **45**, 1115, 1417, 1666, (1923); **46**, 1577 (1924).

[9] Cf. J. Modiano and J. C. Paraud, *Compt. rend.*, **241**, 500 (1955).

[10] G. F. Smith and H. H. Bliss, *J. Am. Chem. Soc.*, **53**, 2091 (1931).

TABLE I
Irreversible Indicators for Bromate Titrations

B *C.I.* No.	Commercial name	Color change	Preparation Per Cent in water[a]
185	Brilliant ponceau 5R	Dark red–colorless	0.2
246	Naphthol blue black	Blue–colorless	0.1
678	Fuchsine	Reddish yellow–colorless	0.2
88	Bordeaux	Red–colorless	0.1

[a] 0.1–0.2 ml. of indicator used.

Hahn[13] has recommended fluorescein, which is converted to eosin at the end-point. Fluorescein reacts slowly with free bromine, and so there is less chance of the indicator being irreversibly changed owing to local concentrations of bromine before the end-point is reached.

Several other dyestuffs have been recommended. Gotô[13] used rhodamine B for the titration of tin(II) with bromate. Benzopurpurin 4B or B has been used similarly.[14] Several other dyestuffs, including some of those examined by Smith and Bliss, were recommended by Sotgia-Rovelli.[15] It is doubtful if any of these have advantages over methyl orange or those finally recommended by Smith and Bliss.

Starch-iodide has been used as indicator;[16] the blue color disappears at the end-point. Winkler[17] added 2 drops of a saturated iodine solution and carbon tetrachloride; the color disappears at the end-point, owing to oxidation of the iodine.

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[11] G. F. Smith and R. L. May, *Ind. Eng. Chem., Anal. Ed.*, **13**, 460 (1941).

[12] H. Nissenson and P. Siedler, *Chem. Ztg.*, **27**, 749 (1903).

[13] F. L. Hahn, *Ind. Eng. Chem., Anal. Ed.*, **14**, 571 (1942); cf. H. Gotô, *Science Repts., Tôhoku Imp. Univ., First Ser.*, **29**, 446 (1940).

[14] T. G. Ralkhinshtein, *J. Appl. Chem. U.S.S.R.*, **8**, 1470 (1935).

[15] T. Sotgia-Rovelli, *Boll. chim. farm.*, **74**, 265 (1935).

[16] G. Charlot, *Bull. soc. chim.*, **1941**, 227; cf. Y. D. Gnesin, A. I. Gengrinovich, and E. S. Yakover, *Zhur. Anal. Khim.*, **2**, 61 (1947).

[17] L. W. Winkler, *Z. anorg. Chem.*, **28**, 477 (1915).

Szebellédy and Schick,[18] were the first investigators to find a satisfactory reversible indicator for titrations with bromate. They added selenious acid to an arsenite solution and formed colloidal red selenium. At the end-point the red selenium was reoxidized to selenious acid. Szebellédy and his coworkers later recommended osmic acid[19] and gold salts[20] as reversible inorganic indicators, but these, like selenium, are now only of academic interest in view of the availability of better reversible organic indicators. Other inorganic indicators have been recommended and reference will be made to them later in the appropriate place.

The first reversible organic indicator, α-naphthoflavone, for bromate titrations was described independently by Uzel[21] and by Schulek.[22] This indicator is one of the best available (see p. 507). Later Schulek and Rózsa[23] recommended *p*-ethoxychrysoidine which, besides being a reversible bromometric indicator, also serves as an acid-base, adsorption and general redox indicator. This is also one of the best bromometric indicators (see p. 508).

Schulek and Somogyi[24] synthesized and examined some thirty azo dyestuff related to *p*-ethoxychrysoidine. Ten of these were found to be suitable as bromometric indicators but apparently had no advantage over *p*-ethoxychrysoidine. Some relationships were established between indicator properties and structural characteristics.

Quinoline yellow, proposed by Belcher,[25] is also a very satisfactory reversible indicator (see p. 508).

Ferroin can be used under certain circumstances,[26] but it is necessary to add a mercuric salt to prevent the free bromine from destroying it. The indicator change then becomes so sluggish that it is necessary to add both osmic acid and sodium vanadate as catalysts, to heat to 40–50° C. and to allow an interval of 40–50 seconds between drops near the end-point. It may also be noted that Modiano and Paraud[9] claimed that *N*-phenylanthranilic acid and *N*-methyldiphenylaminesulfonic acid may be used as indicators when mercuric salts are present, but they state that ferroin and diphenylaminesulfonic acid are destroyed.

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[18] L. Szebellédy and K. Schick, *Z. anal. Chem.*, **97**, 186 (1934); cf. *Chem. Abstr.*, **28**, 1949 (1934).

[19] L. Szebellédy and W. Madis, *Mikrochim. Acta*, **1**, 226 (1937).

[20] *Idem, ibid.*, **3**, 1 (1938); cf. R. Belcher and R. Goulden, *Ind. Chemist*, **26**, 32, 81, (1950). (These papers give details of the use of these and other indicators not in general use.)

[21] R. Uzel, *Collection Czech Chem. Comms.*, **7**, 380 (1935).

[22] E. Schulek, *Z. anal. Chem.*, **102**, 111 (1935); cf. *Chem. Abstr.*, **29**, 3934 (1935).

[23] E. Schulek and P. Rózsa, *Z. anal. Chem.*, **115**, 185 (1939).

[24] E. Schulek and Z. Somogyi, *Z. anal. Chem.*, **128**, 398 (1948).

[25] R. Belcher, *Anal. Chim. Acta*, **5**, 30 (1951).

[26] L. Szebellédy and W. Madis, *Z. anal. Chem.*, **114**, 116 (1938–39)

Apomorphine has been used as indicator in the titration of antimony (III).[27] Although the indicator is perfectly reversible, the color change is feeble.[28] The triphenylmethane dyestuff, rubrophen, has also been recommended,[29] but the reversibility is poor and some destruction of the indicator occurs.

Raĭkhinshteĭn and Kocherigina[30] have established conditions whereby fuchsine will act reversibly in titrations of arsenite, the titration being done at the boiling point. The end-point from red to orange is sharp and quite reversible, but some destruction takes place, for the change becomes less defined each time the end-point is repassed.[28]

TABLE II

Recommended Reversible Indicators

Indicator	Stock solution	Drops per titration	Color change Unbrominated	Brominated
α-Naphthoflavone	0.5% ethanolic	5–10	Greenish opalescence	Rust-brown
p-Ethoxychrysoidine hydrochloride	0.1% aqueous	1–2	Red	Yellow
Quinoline yellow	0.5% aqueous	8	Yellow	Colorless

Standard Solutions: Potassium bromate is a standard substance and can easily be obtained in a pure state by recrystallization from water; purity tests have already been considered (p. 236). Smith[8] recommended barium bromate as an alternative standard substance and also described the use of basic mercuric bromate, $Hg(OH)BrO_3$, for the same purpose. The high stability of standard solutions of potassium bromate was noted by Feit and Kubierschky. Their finding was confirmed by many later investigators; for example,

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[27] L. Szebellédy and K. Sik, *Z. anal. Chem.*, 108, 81 (1937).

[28] R. Belcher, *Anal. Chim. Acta*, 3, 578 (1949).

[29] L. Szebellédy and W. Madis, *Z. anal. Chem.*, 114, 197 (1938–39).

[30] T. G. Raĭkhinshteĭn and T. V. Kocherigina, *Zhur. Anal. Khim.*, 2, 173 (1947).

Van Dame[31] stated that during one year the titer varied by only 1 part in 1000.

To prepare a standard solution of potassium bromate, it is sufficient simply to weigh the pure compound exactly, because the bromate is a primary standard; if, however, it is considered necessary to check it, it may be standardized iodometrically or against arsenious oxide.

Preparation of 0.1N Potassium Bromate: Dry the pure product at 180°C. for 1–2 hours. Weigh 2.784 g., dissolve in water, and dilute to 1 liter.

2. Determination of Inorganic Compounds. ***Trivalent Arsenic:*** Györy[7] titrated arsenic(III) with potassium bromate in a medium varying between 0.25 and 1N in hydrochloric acid at the start of the titration; he used methyl orange as indicator.

$$2BrO_3^- + 3As_2O_3 \longrightarrow 2Br^- + 3As_2O_5$$

Later investigators have used other concentrations and some prefer to heat to 50–60°C. or even higher temperatures[32] to accelerate the reaction. Györy also stated that better end-points were obtained when potassium bromide was not added to the test solution.

The minimum acidity at the end-point is now generally agreed to be approximately 1.2N in hydrochloric acid (cf. Györy) but various figures, ranging from 2.0N[33] to 3.5N,[34] have been quoted for the maximum acidity when methyl orange is used as indicator. Smith[34] showed that the range he recommends for the initial acid concentration (1.6–3.5N), which is also suitable for indigo carmine or naphthol blue black, gives satisfactory results at a working temperature of 25°C. This has also been the experience of the present authors. Smith and May[11] state that bordeaux, brilliant ponceau 5R, and naphthol blue black are satisfactory for the titration of arsenic or antimony at room temperatures in the presence of 20 per cent of hydrochloric acid.

Procedure: Transfer the solution containing arsenic(III) (30–100 mg. of As) to a 250 ml. Erlenmeyer flask, add sufficient water to bring the volume to about 50 ml. and 15 ml. of concentrated hydrochloric acid, and dissolve about 0.5 g. of potassium bromide in this solution. Add 2 drops of 0.1 per cent methyl orange or 0.2 per cent naphthol blue black indicator and titrate with 0.1N bromate solution, taking care to shake the flask vigorously during the addition to avoid local excesses. As the end-point is approached, allow 20–30 seconds between each drop until the color changes from red to colorless or from green to a faint pink. If the indicator fades before the end-point is reached, add 2 more drops. Another drop of indicator may be added at the end-point; if this fades one can be sure that the true end-point has been obtained.

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[31] H. C. Van Dame, *J. Assoc. Offic. Agr. Chemists,* **31**, 572 (1948); cf. *idem, ibid.*, **30**, 502 (1947); M. L. Yakowitz, *ibid.*, **18**, 505 (1935).

[32] Cf. H. Nissenson and A. Mittasch, *Chem. Ztg.*, **28**, 184 (1903).

[33] T. Nakazono and S. Inoko, *Science Repts. Tôhoku Imp. Univ. First Ser.*, **26**, 303 (1937); cf. P. Jannasch and T. Seidel, *J. prakt. Chem.*, **91**, 133 (1915); J. M. Schreyer, G. W. Thompson, and L. T. Ockerman, *Anal. Chem.*, **22**, 691 (1950).

[34] G. F. Smith, *J. Am. Ceram. Soc.*, **29**, 143 (1946); D. J. Kew, M. D. Amos, and M. C. Greaves, *Analyst*, **77**, 488 (1952).

Notes: (1) The indicator blank is negligible at these concentrations.

(2) Indigo sulfonic acid or methyl red may replace the above indicators.

(3) There is no warning of the approach of the end-point, hence it is very convenient to use a titration thief unless the end-point is known approximately. The addition of bromate may then be made more rapidly until the premature end-point is obtained. After the titration thief has been washed and removed, more indicator is added and the titration is completed by slow dropwise addition of titrant.

(4) If fluorescein is used as indicator,[13] add 1 drop of a 0.1 per cent aqueous solution of the sodium salt for each 10 ml. of test solution. Allow 15 seconds between drops near the end-point; the change is from greenish yellow to red-brown. The solution may be heated to 40–50°C. if desired.

(5) Various methods for the separation of arsenic and antimony are considered later (p. 516). Přibil and Čihalik[35] state that arsenic(III) can be titrated preferentially in the presence of iodine monochloride. Sufficient hydrochloric acid is added to give 25–30 per cent of concentrated acid, then 10 ml. of 0.005M iodine monochloride is added and the solution is titrated with 0.1N bromate. Sulfuric acid interferes slightly if more than 10 ml. per 100 ml. of solution is present.

Procedure with α-Naphthoflavone as Indicator:[36] Proceed as in the previous method but add only 6–7 ml. of concentrated hydrochloric acid. Add 5–10 drops of 0.5 per cent ethanolic α-naphthoflavone solution. Titrate with 0.1N bromate solution until the color changes from a slightly green opalescence to rust-brown.

Notes: (1) It is important to titrate slowly near end-point, for the color change is somewhat sluggish. An accuracy of 0.2 per cent is possible.

(2) The indicator correction is usually negligible when 0.1N solutions are used, but samples of α-naphthoflavone appear to vary in purity; if an impure sample should be obtained, it is well to check if there is an indicator blank. The color change may not then be so intense but a further addition of indicator will usually improve matters.

(3) An ethanolic solution of α-naphthoflavone forms a colloidal precipitate when it is added to an aqueous solution and the color change takes place on the surface of the colloidal particles. The more indicator which remains in colloidal suspension, the more pronounced is the color change.

(4) If the end-point is overshot, standard arsenite solution may be added and the end-point reapproached.

(5) Schulek[37] titrates in a sulfuric acid medium.

Procedure: To about 20 ml. of test solution add 10 ml. of 1:1 sulfuric acid,

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[35] R. Přibil and J. Číhalík, *Chem. Listy*, **44**, 224 (1950).

[36] R. Uzel, *Collection Czech Chem. Communs.*, **7**, 380 (1935).

[37] E. Schulek, *Z. anal. Chem.*, **102**, 111 (1935).

0.2 g. of potassium bromide, and 2 drops of 0.5 per cent α-naphthoflavone indicator. Titrate as above. Schulek states that the sensitivity of the indicator is reduced when more than 5 per cent of hydrochloric acid is present. However, this may be overcome by adding more indicator.

Procedure with p-Ethoxychrysoidine as Indicator:[38] To the test solution add 5 ml. of concentrated hydrochloric or sulfuric acid, 1 g. of potassium bromide, and 1–2 drops of 0.1 per cent aqueous *p*-ethoxychrysoidine hydrochloride, and dilute to about 50 ml. with water. Titrate with 0.1*N* bromate solution until the red color turns to a more intense red and then to yellow.

Notes: (1) The original color is restored when more arsenite is added; however, the intensity becomes less at each reversal owing to slight destruction.

(2) The titration may be done with 0.01*N* bromate solution; a 0.05 per cent indicator solution should then be used. The results are accurate to ±0.04 ml. of titrant.

(3) An ethanolic solution of *p*-ethoxychrysoidine may be used in place of the aqueous solution of the hydrochloride. Some samples have been found to be impure and may give a small blank value. Accordingly, it is advisable to determine this on each batch of indicator. Pure samples appear to have a negligible blank, but impure samples may give up to 0.03 ml. of 0.1*N* bromate.

(4) Quinoline yellow[25] may be used in place of *p*-ethoxychrysoidine under exactly similar conditions; 8 drops of a 0.5 per cent aqueous solution are added. The indicator changes sharply from yellow to colorless at the end-point. If the approximate end-point is known, it is advisable to delay the addition of indicator until about 1–2 ml. from the end-point. When a solution of unknown concentration has to be titrated, 4 drops of indicator may be added at the start of the titration and a further 4 drops when the color begins to fade.

Quinoline yellow is a commercial dye of variable composition; hence it is advisable to determine the indicator blank on each new batch.

Applications of the Arsenite Titration: Several determinations are possible where an excess of a standard arsenite solution is allowed to react with the appropriate substance and is then back-titrated with bromate solution. Bacho[39] determined permanganate, manganese dioxide, barium peroxide, chlorates, hypochlorites, and chromates in this way. Similar methods have been described by many later investigators. Bacho found that the following losses of arsenic can occur when solutions containing arsenious chloride and various concentrations of hydrochloric acid are boiled. Up to 12.8 per cent hydrochloric acid, no loss occurred when the solution was boiled for 1 hour; with 15 per cent of acid there was a loss of 0.5 per cent, and with 20 per cent of acid a 50 per cent loss.

Chlorate: Van der Meulen[40] noted the favorable influence of osmic acid on the oxidizing action of chlorate. He found that arsenious acid in slightly acid solution was rapidly oxidized on heating.

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[38] E. Schulek and P. Rózsa, *Z. anal. Chem.*, **115**, 185 (1939).

[39] F. de Bacho, *Ann. chim. appl.*, 12, 153 (1919).

[40] J. H. van der Meulen, *Chem. Weekblad*, **28**, 258 (1931); cf. K. Peters and E. Deutschlander. *Apoth. Ztg.*, **41**, 594 (1926).

Procedure (in absence of iodine compounds): To 50 ml. of 0.1*N* arsenious acid, add 10 ml. of *N* hydrobromic acid (or 10 ml. of *N* hydrochloric acid and about 200 mg. of potassium bromide), 5–45 ml. of 0.1*N* chlorate (*M*/60), and 3 drops of 0.05 per cent osmic acid solution. Heat the mixture on the water bath to 85–90°C. for several minutes, and titrate with potassium bromate solution, using 1 ml. of 0.1 per cent methyl orange as indicator. The osmic acid also catalyzes the oxidation of methyl orange, so that more indicator must be added if necessary. The end-point is thus not exactly the same as the equivalence point and it is advisable to repeat the determination adding the indicator about 1–2 ml. before the end-point.

Note: The back-titration of the excess of arsenite with bromate does not proceed very smoothly. It is also possible to cool the solution, neutralize with excess of bicarbonate, and titrate the arsenious acid with iodine.

Hydrogen Peroxide:[41] *Procedure:* To 10 ml. of approximately 0.1*N* hydrogen peroxide solution add 25 ml. 0.1*N* arsenite solution and 3–5 ml. of 4*N* sodium hydroxide solution. After 1 minute, add 10–12 ml. of concentrated hydrochloric acid and 50 ml. of water, heat nearly to boiling and titrate with 0.1*N* bromate solution; methyl orange is used as indicator.

Notes: (1) Magnesium, calcium, barium, and zinc peroxides may be determined similarly; 0.1–0.3 g. is dissolved in a few ml. of dilute hydrochloric acid and excess of arsenite is added. The solution is made alkaline, acidified after 1–2 minutes, and then titrated as above.

For the determination of sodium peroxide, 20–25 ml. of saturated barium hydroxide solution is added to 0.15–0.3 g. and, after 10 minutes, 50 ml. of arsenite solution is added. The precipitate is dissolved in hydrochloric acid, the solution is made alkaline, reacidified after 1–2 minutes, and then titrated.

Persulfate:[41] *Procedure:* Add excess of 0.1*N* arsenite (50 ml.) to 0.3 g. of the compound and make the solution slightly alkaline. Heat just to boiling and then set aside for 1 minute. Acidify with 10 ml. of 2.5*N* hydrochloric acid and titrate with bromate as above.

Note: Perborate may be determined by heating 0.2 g. with 25 ml. of 0.1*N* arsenite solution just to boiling. Hydrochloric acid (15 ml.) is then added and the solution is titrated with 0.1*N* bromate solution, methyl orange being used as indicator.

Determination of Caro's Acid, Persulfuric Acid and Hydrogen Peroxide in Presence of Each Other: Gleu[42] found that Caro's acid is quantitatively reduced by bromide in slightly acidic solution:

$$H_2SO_5 + 2HBr \longrightarrow H_2SO_4 + H_2O + Br_2$$

The reaction is hastened by the addition of arsenious trioxide which removes the bromine produced. Hydrogen peroxide and persulfuric acid are not attacked under the conditions given. After the back-titration the peroxide can be titrated with permanganate in the presence of sufficient manganous sulfate. Finally persulfate is determined by reducing with arsenic trioxide in hot solution and the excess is back-titrated with bromate.

Procedure. I. Determination of Caro's Acid: To the solution of the three substances containing about 10–20 ml. of 2N sulfuric acid per 50 ml., add a measured excess of 0.1N arsenic trioxide and then 5 ml. of N potassium bromide. After 1–2 minutes, titrate dropwise with 0.1N potassium bromate until the yellow color of free bromine appears permanently. After 1 minute back-titrate the last residue of bromine with arsenious trioxide until the yellow color disappears. (Probably methyl orange or methyl red could be used as indicator.)

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[41] E. Rupp and G. Siebler, *Pharm. Zentralhalle*, **66**, 193 (1925).

[42] K. Gleu, *Z. anorg. u. allgem. Chem.*, **195**, 61 (1931).

II. Determination of Hydrogen Peroxide: To the titrated solution add 5 ml. of 4N manganous sulfate and titrate with 0.1N potassium permanganate. (The end-point is observed by the appearance of free bromine; probably methyl orange could be used as indicator.)

III. Determination of Persulfuric Acid: After the titration with permanganate, add an excess of 0.1N arsenic trioxide and 10 ml. of 20N (1:1) sulfuric acid. Boil for 10 minutes. Back-titrate the excess of arsenic trioxide with 0.1N bromate solution.

Note: Isida and Yukawa[43] described methods for the determination of hydrogen peroxide and persulfuric and permonosulfuric acids in admixture. The titrations are done potentiometrically.

Carbon Monoxide: Winkler[44] used the bromine titration with arsenious oxide for the semimicro determination of carbon monoxide in air. The method is based on the reduction of palladous chloride.

$$PdCl_2 + CO \longrightarrow Pd + COCl_2$$

$$COCl_2 + H_2O \longrightarrow CO_2 + 2HCl$$

The separated metallic palladium is converted to palladous bromide with excess of bromine, which is back-titrated with arsenious acid using iodine and carbon tetrachloride as indicator.[45] The original papers should be consulted for details.

Other Determinations: Kubina[46] determined *arsine* by drawing a known volume of gas into an evacuated flask containing a standard solution of bromate and bromide. After acidifying with sulfuric acid and shaking, excess of standard arsenite was run in and then back-titrated with standard bromate solution.

Lead in alloys has been determined by precipitating as lead chromate with a standard dichromate solution, and determining the excess by reducing with standard arsenite solution and back-titrating with 0.1N bromate.[47]

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[43] T. Isida and M. Yukawa, *J. Soc. Chem. Ind. Japan*, **43**, Supplement, 46 (1940).

[44] L. W. Winkler, *Z. anal. Chem.*, **97**, 18 (1934); **100**, 321 (1935).

[45] L. W. Winkler, *Z. angew Chem.*, **28**, 480 (1915); *Z. anal. Chem.*, **102** 9 (1935).

[46] H. Kubina, *Z. anal. Chem.*, **76**, 39 (1929).

[47] J. H. van der Meulen, *Chem. Weekblad*, **45**, 653 (1949).

Potassium ferrate may be determined by reducing with an excess of arsenite and back-titrating with bromate.[48] The original papers should be consulted for details.

Determination of Arsenic in Organic Compounds: Schulek and Villecz[49] have developed a simple method for the macro and micro determination of arsenic in organic compounds.

Procedure. Macro. Weigh out a sample corresponding to 10–100 mg. of arsenic. Transfer the finely powdered compound to a 100 ml. hard glass flask and cover with 2–3 ml. of 30 per cent hydrogen peroxide. Shake, carefully add 10 or 5 ml. of concentrated sulfuric acid, and shake again. The reaction proceeds with vigorous frothing usually to give an immediate colorless solution. If not, add another 1–2 ml. of hydrogen peroxide to bleach the solution. Heat the flask over a small flame and remove any slight yellow color which appears immediately by adding hydrogen peroxide. Continue the heating until fumes of sulfuric acid appear and then boil strongly for 1 minute. Remove the flame. During the decomposition the liquid must in no case be allowed to darken owing to charring of the organic compound because the arsenic acid would then be reduced; under the conditions, volatile arsenic trihalide could be lost if the compound contained chlorine, bromine or iodine originally.

For the reduction, add to the cooled solution, through a long-handled powder funnel, 100 mg. of chloride-free hydrazine sulfate. No hydrazine should remain on the flask walls, otherwise it would remain undecomposed and would be titrated by the bromate. Reheat the solution when the crystals decrepitate and dissolve with the development of nitrogen and sulfur dioxide. To remove the sulfur dioxide, boil the solution vigorously for 10 minutes. Cool thoroughly, add 25 ml. of water, shake, add about 100 mg. of potassium bromide, and titrate with 0.1*N* potassium bromate to a yellow color. According to Winkler[50] this titration can advantageously be carried out without an indicator.

Micro: Use a finely powdered sample corresponding to 0.5–10 mg. of arsenic. For liquids if possible only 1–2 g. should be used. Larger amounts should be concentrated before the determination, which is best done in alkaline solution. If more than 50 mg. of organic compound is to be decomposed, the oxidation is best done in a decomposition flask. For smaller amounts, a 50 ml. glass-stoppered reagent vessel of Jena glass is suitable; the titration is carried out in this vessel.

For the decomposition in the flask, cover the compound with 2–3 ml. of 30 per cent hydrogen peroxide, shake, add 3 ml. of concentrated sulfuric acid, and shake again. Treat the solution as in the macro method, but use only 50 mg. of hydrazine sulfate. After boiling for 10 minutes to remove sulfur dioxide, cool and transfer the concentrated solution to a reagent vessel with three 5 ml. portions of water. Add 20–30 mg. of potassium bromide, 1 ml. of carbon tetrachloride, and 2 drops of a saturated aqueous solution of iodine. Shake strongly when the iodine dissolves in the solvent layer. Titrate the arsenious acid with 0.01N bromate solution, shaking vigorously after each addition. The violet color at first fades with decreasing acid concentration because of iodide formation, then deepens as the end-point approaches and finally changes very sharply to colorless. Read the burette and add another drop of bromate solution. If the end-point was correctly reached the solvent layer should turn yellow because of separated bromine. From the amount of potassium bromate, subtract the amount necessary for the formation of iodine bromide. This averages 0.05 ml., but it is better to run a blank on all the reagents which are used.

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[48] J. M. Schreyer, G. W. Thompson, and L. T. Ockerman, *Anal. Chem.*, 22, 691 (1950).

[49] E. Schulek and P. von Villecz, *Z. anal. Chem.*, 76, 81 (1929).

[50] L. W. Winkler, *Z. Untersuch. Nahr. Genussm.*, 43, 202 (1922).

Notes: (1) For the purity of the reagents and the purification of carbon tetrachloride, consult the paper of Winkler.[51]

(2) For the determination of arsenic in presence of other metals, such as calcium, strontium, barium, iron, lead, and mercury, consult the original paper of Schulek and Villecz.[49] If iron is present, the solution becomes yellow because of ferric iron and must be bleached with sufficient phosphoric acid. Also for the macro decomposition only 5 ml. of concentrated sulfuric acid should be used. The same holds for the presence of lead. For the micro method, lead sulfate should be filtered off on a cotton wool pad because the lead forms lead iodide with the iodine indicator. Iodine cannot be used as indicator in presence of mercury because of mercuric iodide formation, but this causes no trouble in the macro method. The method described by Schulek and Villecz appears to be one of the simplest and most elegant methods for the determination of arsenic in organic compounds. For the full details, the original paper should be consulted.

(3) Later, Schulek and Wolstadt[52] used the same method for the determination of antimony in organic compounds. A modification is also described whereby both arsenic and antimony can be determined on the same sample.

(4) Sloviter *et al.*[53] decomposed organic compounds with sulfuric and nitric acids and reduced with sodium hypophosphite to give elemental arsenic. This is filtered off, dissolved in an excess of standard bromate-bromide solution, treated with potassium iodide, and liberated iodine is titrated with standard arsenite in the presence of starch indicator. The decomposition procedure must be modified for cacodylic acid compounds.[54]

Banks *et al.*[55] examined several decomposition procedures; in all cases they recommended titration with bromate and they used either methyl orange as indicator or a platinum–calomel system. Wyatt[56] determined arsenic in micro amounts after decomposing with a mixture of sulfuric acid and ammonium sulfate. He titrated with $0.01N$ bromate and used α-naphthoflavone as indicator. Antimony was determined likewise after the addition of tartrate.

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[51] L. W. Winkler, *Z. angew. Chem.*, **28**, 480 (1915).

[52] E. Schulek and R. Wolstadt, *Z. anal. Chem.*, **108**, 400 (1937).

[53] H. A. Sloviter, W. M. McNabb, and E. C. Wagner, *Ind. Eng. Chem., Anal. Ed.*, **14**, 516 (1942).

[54] V. Levine and W. M. McNabb, *Ind. Eng. Chem., Anal. Ed.*, **15**, 76 (1943).

[55] C. K. Banks, J. A. Sultzaberger, F. A. Maurina, and C. S. Hamilton, *J. Am. Pharm. Assoc.*, **37**, 13 (1948).

[56] P. F. Wyatt, *Analyst*, **80**, 368 (1955).

Tsuda and Sakamoto[57] decomposed with sulfuric acid-hydrogen peroxide mixture and reduced with hydrazine. They tried α-naphthoflavone, *p*-sulfonamido chrysoidine hydrochloride, *p*-ethoxychrysoidine, methyl red, methyl orange, and indigo carmine as indicators for the bromate titration. They considered α-naphthoflavone to be the best indicator.

Antimony: Győry[7] determined antimony by the same procedure he used for arsenic (p. 506). The method was adopted by many later workers, particularly for the determination of antimony in alloys and ores. Nissenson and Siedler[58] determined antimony in crude lead. They preferred to titrate the solution at elevated temperatures and used methyl orange or indigo sulfonic acid as indicator which was only added when the end-point was approached. These investigators made a very full examination of Győry's method.[59]

Procedure: Proceed exactly as in the titration of arsenic(III); the same irreversible indicators may be used (p. 506).

Notes: (1) When any of the reversible indicators (pp. 507–508) is used, it is necessary to add 0.5–1.0 g. of Rochelle salt to prevent hydrolysis of antimony at the lower acid concentrations.

(2) Antimony in organic compounds may be determined as follows.[60]

Procedure: Transfer the sample, containing about 0.1 g. of antimony, to a 400 ml. beaker. Add 2 ml. of water, 5 ml. of concentrated sulfuric acid, and 2 ml. of concentrated nitric acid. Heat on a sand bath to fumes of sulfuric acid, cool, add 1 ml. of nitric acid, and take to fumes again. Repeat twice. If any organic matter remains, repeat the oxidation until the solution is colorless. Cool, add 5 ml. of water, and take to fumes. Repeat twice. A white deposit should now be present in the solution. Add 20 ml. of a bromine-hydrobromic acid mixture (10 ml. of bromine in 100 ml. of hydrobromic acid heated gently to dissolve the bromine) and warm gently to dissolve the deposit. Cool, add 150 ml. of a saturated solution of sulfurous acid, and set aside for 1 hour. Add 10 ml. of hydrochloric acid and 100 ml. of water, and boil out the sulfur dioxide. The volume must be greater than 150 ml. Add methyl orange indicator and titrate the hot solution with $0.05N$ bromate.

If desired, antimony may be first separated as the sulfide; the dissolution of the precipitate, the reduction and titration follow the above procedure closely.

(3) Antimony may be separated as sulfide by precipitation with thioacetamide.[61] The precipitate is dissolved and titrated in the usual way.

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[57] K. Tsuda and S. Sakamoto, *J. Pharm. Soc. Japan*, **61**, 217 (1941); *Chem. Abstr.*, **44**, 8819 (1950).

[58] H. Nissenson and P. Siedler, *Chem. Ztg.*, **77**, 749 (1903); cf. J. B. Duncan, *Chem. News*, **95**, 49 (1907).

[59] Cf. E. Schmidt, *Chem. Ztg.*, **34**, 453 (1910); O. Collenberg and G. Bakke, *Tids. Kjemi Bergvesen*, **3**, 93, 104 (1923).

[60] N. T. Wilkinson, *Analyst*, **78**, 165 (1953).

[61] H. Flaschka and H. Jakobljerich, *Anal. Chim. Acta*, **4**, 247 (1950).

Determination of Antimony in Ores and Alloys: Antimony in stibnite may be determined by titration with bromate.[62] Preliminary separation as sulfide is said to be unnecessary. The method has been used extensively in the analysis of alloys.[63] Wooten and Luke[64] indicated that several precautions must be taken during the dissolution of lead-antimony alloys to ensure that all the antimony is in the trivalent form. The oxidation is catalyzed by copper ions. Luke[65] later recommended reducing with sulfurous acid in the analysis of tin-base alloys.

Procedure: Transfer 1 g. of the finely divided sample (free of metallic iron) to a dry 500 ml. Erlenmeyer flask. Add 10 ml. of sulfuric acid and heat (without a cover) first on a hot plate and then on a Tirrill flame until complete dissolution of the sample is attained and copious white fumes are evolved. During the initial treatment with acid, avoid heating the sample on a plate that is too hot; otherwise the sample may melt and complete dissolution will become very difficult. Cool. Add 10 ml. of water and 3 or 4 grains of 12 mesh silicon carbide (to minimize bumping). Add 50 ml. of hydrochloric acid and warm the solution for a few minutes to dissolve all salts. Adjust the temperature to approximately 50°C. Add 25 ml. of sulfurous acid (6 per cent) and place the flask on a hot plate with a surface temperature of 275–300°C. Boil the solution without a cover until the volume is reduced to 60 ± 5 ml., remove from the plate, and dilute to 350 ml. with boiling water. Pass a fairly rapid stream of air or oxygen through the solution for 5 minutes. Titrate at 85–90°C. with 0.1*N* potassium bromate solution, and 3 drops of 0.1 per cent methyl orange as indicator.

Small Amounts of Arsenic, Antimony, and Tin in Lead and Lead Alloys: Luke[66] dissolves the alloy in nitric acid and separates arsenic, antimony, and tin as hydrated oxides by coprecipitation with manganese dioxide. After separation from the lead, the metal oxides are converted to sulfates, and arsenic and antimony are reduced to the trivalent state; arsenic is distilled as chloride and titrated. In the residue, antimony is titrated with 0.01*N* bromate. Finally, tin is reduced with lead and titrated with standard iodine solution (p. 321).

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[62] E. Rupp, G. Siebler, and W. Brachmann, *Pharm. Zentralhalle*, 66, 33 (1925); cf. Y. A. Chernikov and P. A. Kolodub, *Zavodskaya Lab.*, 9, 467 (1940).

[63] H. W. Rowell, *J. Soc. Chem. Ind.*, 25, 1181 (1906); G. Oesterheld and P. Honegger, *Helv. Chim. Acta*, 2, 398 (1919); H. Biltz, *Z. anal. Chem.*, 66, 267 (1925); C. W. Anderson, *Ind. Eng. Chem., Anal. Ed.*, 6, 456 (1934); 11, 224 (1939); C. Cimerman and M. Ariel, *Anal. Chim. Acta*, 7, 441 (1952) (microscale); L. Bloch, *Chem. Weekblad*, 51, 548 (1955).

[64] L. A. Wooten and C. L. Luke, *Ind. Eng. Chem., Anal. Ed.*, 13, 771 (1941).

[65] C. L. Luke, *Ind. Eng. Chem., Anal. Ed.*, 16, 448 (1944).

[66] C. L. Luke, *Ind. Eng. Chem., Anal. Ed.*, 15, 625 (1943).

Procedure: Weigh 50 g. of the milled sample into a 500 ml. Erlenmeyer flask, add 150 ml. of water and 50 ml. of nitric acid, and heat gently to dissolve the sample. Dilute to 300 ml. and heat to boiling to expel brown fumes. Add 10 ml. of potassium permanganate (2 per cent solution) to oxidize the arsenic, antimony, and tin. Add 20 ml. of manganese nitrate (10 per cent solution), and boil gently for 2 minutes. (The manganese nitrate must not be added before the potassium permanganate.) Filter hot through a rapid paper and wash well with hot water to remove as much lead nitrate as possible. Reserve the filtrate. Return the paper to the 500 ml. Erlenmeyer flask, add 15 ml. of sulfuric acid and 35 ml. of nitric acid, and heat to gentle boiling to destroy the filter paper.

Add 35 g. of pure ammonium sulfate dissolved in 100 ml. of water to the reserved filtrate and cool to room temperature. Filter through close paper on a Büchner funnel, refiltering if the solution is not clear. Wash once or twice with water. Discard the lead sulfate. Neutralize with ammonium hydroxide to the blue color of copper ammonium ion, or to litmus if the lead sample does not contain copper. Add 15 ml. of ammonium hydroxide in excess, heat to boiling, add 10 ml. of ammonium persulfate (10 per cent solution), and boil vigorously for 1 minute. Filter through a rapid paper. Wash the precipitate onto the paper. (Ignore the small amount of precipitate which cannot be washed from the walls of the beaker.) Wash the precipitate 3 or 4 times with hot water and discard the filtrate. Place the paper in the 500 ml. flask with the first paper. The flask now contains all the arsenic, antimony, and tin, plus some manganese, lead, and traces of other elements such as iron and copper.

Add 35 ml. of nitric acid and boil gently to destroy all carbonaceous material. Take to copious white fumes to expel nitric acid and to dissolve all lead sulfate. (Incomplete solution of the lead sulfate indicates that the manganese dioxide precipitates have not been adequately washed. Sufficient sulfuric acid to ensure complete solution must be added before proceeding.) Cool, add 100 mg. of hydrazine sulfate and 3 g. of potassium acid sulfate, and wash down the flask with about 10 ml. of water, making sure that no hydrazine sulfate remains on the walls. Boil to expel the water. Take to copious white fumes over a flame and fume strongly for 30–60 seconds to ensure complete expulsion of sulfur dioxide.

Cool and add 10 ml. of water. Cool to 25°C., add 50 ml. of hydrochloric acid, and a few grains of 12 mesh silicon carbide to prevent bumping. Stopper with a distillation head, and heat to boiling on a hot plate, catching the distillate in 300 ml. of water in a 400 ml. beaker. (It is not necessary to keep this water cold, since arsenic trichloride cannot be distilled from solutions containing less than 16 per cent of hydrochloric acid.) Boil the solution at a moderate rate until the temperature of the vapor rises to 105° C. When this temperature is attained, remove the flask from the plate and detach the distillation head. Dilute the solution containing the tin and antimony to 275 ml. Heat to gentle boiling to dissolve all lead salts. (Failure to dissolve lead salts will lead to low results for antimony. If complete solution is not attained, add 10 g. of sodium chloride and boil to dissolve all salts.) Titrate this solution, and that containing the arsenic, at 95° C. with standard potassium bromate, using methyl orange as indicator. Provide for blank correction.

$$\text{ml. of } 0.01N \text{ KBrO}_3 \times 0.001218 = \text{per cent antimony}$$

$$\text{ml. of } 0.01N \text{ KBrO}_3 \times 0.0007490 = \text{per cent arsenic}$$

Antimony in Presence of Arsenic: When these elements are both present in the trivalent form, their sum can be determined by titration with bromate. According to McKay,[67] the pentavalent antimony in hydrochloric acid solution can be reduced to the trivalent state by shaking with mercury while the arsenic remains unattacked.

$$Sb^{5+} + 2Cl^- + 2Hg \longrightarrow Sb^{3+} + Hg_2Cl_2$$

Procedure: The reduction is carried out in a cylindrical flask of volume about 150 ml. which can be sealed air-tight with a glass stopper. Pipette the test solution, which should be about 3–4N in hydrochloric acid into the flask and dilute to about 75 ml. with 3–4N hydrochloric acid. Add 20–25 ml. of mercury. (Reverse the order of addition if preferred.) Remove the air from the solution by passing a strong stream of carbon dioxide for 10 minutes. Rinse the inlet tube and seal the flask hermetically. Shake mechanically for 1 hour, allow the mercury-calomel mixture to settle, and filter through a close filter. Wash the residue in the flask thoroughly with 1–2N hydrochloric acid. Dilute the filtrate to 200 ml. and titrate.

Notes: (1) The method gives excellent results in the presence of arsenic and stannic acids, tetravalent antimony, lead, cadmium, and bismuth.

(2) Copper salts are reduced to cuprous. After the filtration, pass a strong stream of air through the solution for 30 minutes to reoxidize the cuprous copper and then titrate the trivalent antimony. The results obtained are then a little too low, probably on account of oxidation of antimony induced by the copper system.

(3) The reductor can be quantitatively regenerated after a determination by shaking the hydrochloric acid solution with stannous chloride.

(4) Undoubtedly the silver reductor (p. 14) could be used instead of mercury.

(5) Various distillation methods have been recommended for the separation.[68] The fractional distillation of arsenic, antimony, and tin has been described.[69]

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[67] L. W. McKay, *Ind. Eng. Chem., Anal. Ed.*, 5, 1 (1933).

[68] P. Jannasch and T. Seidel, *J. prakt. Chem.*, 91, 133 (1915); K. K. Järvinen, *Z. anal. Chem.*, 62, 184 (1923).

[69] H. Biltz, *Z. anal. Chem.*, 81, 82 (1930); H Biltz and K. Hoehne, *ibid.*, 99 1 (1934).

Haslam and Wilkinson[70] precipitate elemental arsenic with hypophosphite and then isolate antimony from the filtrate by precipitation as the sulfide. The original papers should be consulted for details.

Tin: Stannous tin can be titrated in the same way as arsenic and antimony. To avoid atmospheric oxidation it is preferable to use an atmosphere of carbon dioxide. Fichter and Müller[71] titrated with standard bromate to the first appearance of free bromine. Oesterheld and Honegger[72] determined tin and antimony in alloys by first titrating trivalent antimony and then reducing stannic tin with metallic zinc. After the metallic tin has been redissolved, the stannous tin is titrated.

Procedure:[72] Dissolve 1 g. of alloy in 20 ml. of concentrated sulfuric acid and boil to drive off sulfur dioxide. The antimony is now in the trivalent and the tin in the quadrivalent form. Cool, dilute cautiously to about 100 ml. with water, add 5 ml. of concentrated hydrochloric acid and methyl orange indicator, and titrate the antimony with $0.1N$ bromate in the usual way. Set aside for 1 hour, filter off the lead sulfate and weigh. Transfer the filtrate to a flask fitted with a Göckel-Contat trap, add 80 ml. of concentrated hydrochloric acid and add three separate portions of 3 g. of zinc turnings. Boil to redissolve the *tin* metal and cool quickly under the tap. Remove the trap, add 0.2 g. of potassium iodide and starch indicator, and titrate with $0.1N$ potassium bromate solution.

Notes: (1) If the tin is more than 30 per cent of the alloy an aliquot of the filtrate should be taken.

(2) Standard potassium iodate (pp. 459, 470) or iodine solutions (p. 319) can be used instead of bromate.

(3) Tin (II) may be titrated in the presence of antimony(III). The oxidation of tin(II) is complete before that of antimony(III) begins under proper conditions of acidity. The end-point is given by the first appearence of the blue starch-iodine color. Even 1 g. of antimony trichloride does not interfere with the titration of 0.25 g. of tin.

(4) Ferjančič[73] prefers to add excess of bromate and to back-titrate iodometrically.

(5) Raĭkhinshteĭn[74] states that the titration of tin(II) is best done in $1.15N$ hydrochloric acid at 30–50°C. Other acidities have been recommended, however; Nakazono[75] recommended $0.4–0.6N$, and Gotô[76] $0.5–1.2N$. Raĭkhinshteĭn used benzopurpurin 4B or B as indicator. Gotô used rhodamine B as indicator. Velich,[77] who modified Fichter and Müller's method, recommended Capri blue.

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[70] J. Haslam and N. T. Wilkinson, *Analyst*, 78, 390 (1953).

[71] F. Fichter and E. Müller, *Chem. Ztg.*, 37, 309 (1913).

[72] G. Oesterheld and P. Honegger, *Helv. Chim. Acta*, 2, 398 (1919).

[73] S. Ferjančič, *Z. anal. Chem.*, 98, 246 (1934).

[74] T. G. Raĭkhinshteĭn, *J. Applied Chem. U.S.S.R.*, 8, 1470 (1935).

[75] T. Nakazono, *Science Repts. Tôhoku Imp. Univ. First Ser.*, 26, 743 (1937).

[76] H. Gotô, *Science Repts. Tôhoku Imp. Univ. First Ser.*, 29, 446 (1940).

[77] V. Velich, *Chem. Listy*, 15, 5, 38, 56 (1921).

(6) Aluminum[77,78] and nickel[77] have also been recommended for reducing tin before the bromate titration.

(7) Portnov[79] precipitates stannic tin with either sodium (*p*-hydroxyphenyl) arsonate or sodium (4-hydroxy-3-nitrophenyl) arsonate. The precipitate is dissolved, treated with an excess of standard bromate, then with standard arsenite, and is finally titrated with the bromate solution. Indigo carmine is used as indicator.

Biltz[80] states that in the Oesterheld and Honegger method the reduction is uncertain because most of the zinc is consumed in reacting with the acid at the high concentration used. This may be overcome by initially using acid of only moderately strong concentration.

Procedure: Transfer the filtrate (see note 1 of previous method) to a narrow-neck 1 liter flask fitted with a Göckel-Contat trap. Add 20 ml. of concentrated hydrochloric acid and 8 g. of zinc foil fragments (2 x 0.2 x 0.12 cm.). Cool in water and shake occasionally. After 20–25 minutes, the zinc has dissolved and the tin has precipitated. Rinse the neck of the flask, add 4 g. of zinc, and replace the trap. After 20 minutes, add 70–80 ml. of concentrated hydrochloric acid to dissolve the zinc residue. Warm gently so that the tin metal dissolves in about 30 minutes. Antimony and copper remain undissolved. Cool under the tap at first without, and then with, shaking. Rinse the stopper and the neck of the flask with a solution containing 100 ml. of water, 0.2 g. of potassium iodide, 5 ml. of starch, and 10 ml. of dilute hydrochloric acid which has been freed from air with a little sodium bicarbonate. Titrate immediately with 0.1*N* bromate solution to the first blue color. It is desirable to run a rough titration first and then to add most of the bromate rapidly to a second solution.

Note: Unless all atmospheric oxygen has been excluded an error is introduced if the theoretical equivalent of tin is used in the calculation; even the bromate solution must be free from oxygen. It is recommended that an empirical titer be obtained by dissolving pure tin in concentrated sulfuric acid and carrying out the complete process.

Cuprous Copper: The titration with bromate proceeds smoothly and gives good results in the absence of air. Reissaus[81] has applied this titration to the determination of bismuth in its salts. The cation is reduced with metallic copper in hydrochloric acid solution in an

$$BiCl_3 + 3Cu \longrightarrow 3CuCl + Bi$$

atmosphere of carbon dioxide. The end-point with methyl orange indicator is from rose to blue because of the cupric ion.

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[78] L. Deutsch, *Ann. chim. anal. et chim. appl.*, 18, 10 (1936).

[79] A. I. Portnov, *Zhur. Anal. Khim.*, 9, 175 (1954).

[80] H. Biltz, *Z. anal. Chem.*, 66, 267 (1925); cf. *idem, ibid.*, 81, 82 (1930).

[81] G. G. Reissaus, *Z. anal. Chem.*, 70, 300 (1927).

Travagli[82] has titrated various cuprous salts in this way and has applied the method to the indirect determination of reducing sugars.

Thallium: The oxidation of thallous salts with bromate is immediate in hydrochloric acid solution. The principle was first used by Sponholz,[83] who titrated with a standard solution of bromine water. Marshall[84] heated the thallous salt with an excess of bromate and hydrochloric acid; the bromine formed was distilled into potassium iodide solution. Both these methods are unattractive. Kolthoff[85] titrated directly with standard bromate and used methyl orange as indicator. Zintl and Rienäcker[86] preferred this procedure or potentiometric detection of the end-point. They state that with methyl orange better end-points are obtained when the titration is done at 50°C. rather than at room temperature.

Procedure: Heat the solution containing the thallous salt (150 ml. containing 5–8 per cent of hydrochloric acid) to 50–60°C. Add methyl orange indicator and titrate with standard bromate solution.

Note: Arsenic(V), antimony(V), tin(IV), copper(II), bismuth, cadmium, lead, and mercury do not interfere. Iron(III) causes low results owing to the reaction

$$2Fe^{3+} + Tl^{+} \rightleftharpoons 2Fe^{2+} + Tl^{3+}$$

and ferrous iron is significantly oxidized by the air under these conditions. The addition of phosphate ion overcomes this, but the end-point is then not so sharp owing to the color of the complex.

Selenium: Coleman and McCrosky[87] determined selenium in selenious acid after precipitating the element by the method of Lenher and Kao.[88] In order to obtain the selenium in an easily reactive form, it is first transformed to selenocyanide, which decomposes in acid medium to give finely divided selenium.

Procedure: Dissolve the washed selenium in 10 ml. of potassium cyanide solution which contains about 3 times the theoretical amount required. Evaporate the solution to dryness. Selenium is thus converted to selenocyanide:

$$CN^{-} + Se \longrightarrow CNSe^{-}$$

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[82] G. Travagli, *Ann. chim appl.*, **30**, 122 (1940).

[83] K. Sponholz, *Z. anal. Chem.*, **31**, 519 (1892).

[84] H. Marshall, *J. Soc. Chem. Ind.*, 19, 994 (1900).

[85] I. M. Kolthoff, *Rec. trav. chim.*, **41**, 172 (1922).

[86] E. Zintl and G. Rienäcker, *Z. anorg. Chem.*, **153**, 276 (1926); cf. G. Rienäcker and G. Knauel, *Z. anal. Chem.*, **128**, 459 (1947).

[87] W. C. Coleman and C. R. McCrosky, *J. Am. Chem. Soc.*, **59**, 1458 (1937).

[88] V. Lenher and C. H. Kao, *J. Am. Chem. Soc.*, **47**, 2454 (1925).

This reaction goes from right to left on acidification. Dissolve the residue in 10 ml. of water and add 2 ml. of 1 per cent gum arabic solution (to keep the selenium in colloidal solution) and 10 ml. of concentrated hydrochloric acid (sp. gr. 1.18). Remove the excess of cyanide by passing air through the solution for 15 minutes.

Titrate with bromate by one of the following methods.

Method (*a*). Titrate with bromate to the disappearance of the red colloidal selenium. The color change is from red through yellow to colorless. With careful titration near the end-point, 13–44 mg. of selenium can be titrated with an accuracy of 0.2 per cent.

$$3Se + 2BrO_3^- + 3H_2O \longrightarrow 3H_2SeO_3 + 2Br^-$$

Method (*b*). Titrate with bromate but near the end-point add sufficient $0.5N$ iodine monochloride solution (preparation, p. 456) to oxidize the selenium:

$$Se + 4ICl + 3H_2O \longrightarrow H_2SeO_3 + 2I_2 + 4HCl$$

and 4 ml. of carbon tetrachloride. (The selenium must have almost quantitatively disappeared; otherwise carbon tetrachloride dissolves selenium and the reaction then proceeds very slowly.) Continue the titration with bromate until the iodine color disappears from the organic solvent layer. The end-point of this method is sharper than that of method (*a*). The acidity must be between 1 and $6N$ at the end-point. The accuracy is 0.2 per cent.

Notes: (1) When the solution contains less than 10 mg. of selenium, the addition of gum arabic can be omitted. Thus 0.6–0.7 mg. of selenium can be titrated with $0.005N$ bromate with an accuracy of 0.3 per cent.

(2) It is possible to dissolve the colloidal selenium in excess iodine monochloride solution and then to titrate the liberated iodine with bromate immediately, using carbon tetrachloride to detect the end-point with an accuracy of 0.2–0.3 per cent.

(3) The titration can also be done with potassium iodate at an acidity of 2–$6N$ hydrochloric acid with an accuracy of 0.2 per cent.

$$5Se + 4IO_3^- + 3H_2O + 4H^+ \longrightarrow 5H_2SeO_3 + 2I_2$$
$$2I_2 + IO_3^- + 6H^+ + 5Cl^- \longrightarrow 5ICl + 3H_2O$$

Potassium dichromate can also be used a titrant if the acidity is at least $8N$ at the end-point and iodine monochloride is present to catalyze the reaction; the accuracy is 0.3 per cent. If the selenium is first dissolved in iodine monochloride and then titrated with dichromate, the results are unsatisfactory. Permanganate or ceric sulfate could not be used as titrant.

(4) Shaver and McCrosky[89] used the bromate method for the determination of the sum of selenium and sulfite. To 25 ml. of the mixture is added 10 ml. of 0.5 per cent starch to keep the selenium in colloidal suspension. Then standard bromate solution is run in until about 1 ml. before the end-point (as determined by a preliminary titration); 70 ml. of $6N$ hydrochloric acid is added and the titration is completed rapidly. A potentiometric end-point is used. The selenium is oxidized to selenious acid, and the sulfite to sulfate. After reaching the end-point, the selenious acid is titrated by the method of Norris and Fay (p. 328).

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[89] R. C. Shaver and C. R. McCrosky, *Ind. Eng. Chem., Anal. Ed.*, 12, 74 (1940).

Selenite: Adams and Gilbertson[90] oxidize selenite to selenate in nitric acid solution with an excess of bromate which is determined with standard arsenious trioxide solution.

Standard 0.1N Potassium Bromate Solution: The bromate is dissolved in water and the solution filled up to the mark using 50 ml. of concentrated nitric acid (sp. gr. 1.42) per liter.

Procedure: To the weighed sample containing 0.1–0.3 g. of selenium dioxide, add an excess of the bromate solution and boil until all the bromine has been expelled. Add from a burette excess standard arsenious trioxide solution to reduce the excess of bromate (if necessary run a preliminary titration). Add 10 ml. of concentrated hydrochloric acid and 2 drops of 0.5 per cent fast red B solution and titrate with bromate solution to colorless. The volume of solution should be kept at about 50 ml. and the final titration should be carried out at or below 80°C.

$$2BrO_3^- + 2H^+ + 5SeO_3^{2-} \longrightarrow Br_2 + 5SeO_4^{2-} + H_2O$$

Notes: (1) A standard bromate solution in water can be used if 0.6–1.5 ml. of concentrated nitric acid is added per 50 ml. of solution.

(2) Certain cations which form insoluble selenates, such as barium and lead, interfere. Other cations which are easily oxidized or reduced, such as ferric and chromic ions, interfere. Colored ions such as copper and nickel make the end-point observation difficult; nevertheless, relatively large amounts of these ions can be present if more indicator is used. Halide ions interfere. Large quantities of alkali and alkaline earth metals, except barium, do not interfere, nor do selenate, sulfate, and tellurate.

Iron: The oxidation of ferrous iron with bromate is comparatively slow especially in the neighborhood of the end-point. Thus, if methyl red or methyl orange is used as indicator in the titration of iron with bromate, the color disappears long before the equivalence point is reached. If more indicator is added after standing for several minutes, a red color is again produced but the method is unsuitable for determination of ferrous iron. Smith and Bliss[91] recommended the addition of a copper salt as catalyst. However,

$$Cu^{2+} + Fe^{2+} \rightleftharpoons Cu^+ + Fe^{3+} \qquad \text{(rapid)} \qquad (1)$$

$$6Cu^+ + BrO_3^- + 6H^+ \longrightarrow 6Cu^{2+} + Br^- + 3H_2O \qquad \text{(rapid)} \qquad (2)$$

the copper also catalyzes the atmospheric oxidation of the ferrous iron because the cuprous ions formed (equation 1) are rapidly reoxidized. To prevent this, arsenate is also added; arsenate oxidizes the cuprous copper, forming arsenious acid, which is stable in air in acid solution and is rapidly oxidized by bromate. Phosphoric acid is also added to lower the oxidation potential of the iron system.

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[90] D. F. Adams and L. S. Gilbertson, *Ind. Eng. Chem., Anal. Ed.*, **14**, 926 (1942).

[91] G. F. Smith and H. H. Bliss, *J. Am. Chem. Soc.*, **53**, 4291 (1931).

Smith and Bliss[91] titrated with a solution of basic mercuric bromate. Kolthoff has found that potassium bromate is equally satisfactory.

$$6Fe^{2+} + BrO_3^- + 6H^+ \longrightarrow 6Fe^{3+} + Br^- + 3H_2O$$

The best end-point is obtained with a 0.1 per cent aqueous solution of naphthol blue black. The advantage of the bromate titration is that various organic compounds, such as tartaric acid, citric acid, and succinic acid, do not interfere, whereas the dichromate and permanganate methods cannot be used in their presence. Alcohol, acetone, sugars, and formic acid also interfere in the bromate titration.

Reagents. Catalyst Solution: Mix 12.5 g. of ammonium arsenate, 0.425 g. of cupric chloride, and 250 ml. of 85 per cent phosphoric acid and dilute to 500 ml. with water.

Procedure: To 25 ml. of the iron solution, add enough hydrochloric acid to give a normality of 1–1.5, 10 ml. of the catalyst solution, and 1 drop of naphthol blue black indicator. Titrate slowly near the end-point and shake well after each addition of the titrant; otherwise the end-point will appear too soon.

Notes: (1) Kolthoff found that the method gives good results in the presence of tartaric acid, citric acid, and succinic acid. In the presence of oxalic acid, however, the end-point appears too quickly because ferrous iron forms an intense yellow-colored complex with this acid and the ferric complex has also a pronounced yellow-brown color. The addition of hydrofluoric acid (instead of phosphoric acid) permits a more satisfactory determination.

(2) Mercuric chloride does not affect the results, so that the method can be used after reduction of ferric iron with stannous chloride and removal of the latter with mercuric chloride (see p. 84). It appears to be possible to apply this method to the determination of iron in organic compounds after complete decomposition of the compound with permanganate in acid solution and reduction with stannous tin.

(3) Szebellédy and Madis[92] titrate at a temperature of 60–70°C., using gold chloride as indicator, with a comparison solution for the end-point.

(4) A back-titration procedure may also be applied.[93]

Procedure: Add 25 ml. of $0.1N$ bromate and 10 ml. of 25 per cent phosphoric acid to 10 ml. of the slightly acid ferrous solution. Stopper the vessel and set aside for 5 minutes. Add 5 ml. of $1N$ potassium iodine solution and 2 drops of 3 per cent ammonium molybdate (as catalyst). After 3 minutes titrate with thiosulfate in the usual way.

Uranium: The direct titration of uranium(IV) with bromate and methyl orange as indicator gives a premature end-point because the reaction is sluggish;[94] catalysts do not help. The addition of an excess of bromate followed by an iodometric back-titration is also unsatisfactory. However, if a ferric solution is added to the uranium solution containing 20 per cent of hydrochloric acid and cupric chloride as catalyst, the ferrous iron so produced may be titrated satisfactorily; methyl orange is used as indicator. The method tends to give high results.

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[92] L. Szebellédy and W. Madis, *Z. anal. Chem.*, **114**, 249 (1938).

[93] I. M. Kolthoff, *Z. anal. Chem.*, **60**, 448 (1921).

Vanadium: Erdey and Mázor[95] determined vanadium(II) by titration with standard bromate. The end-points were detected potentiometrically or with safranine T as indicator. The titration had to be done slowly when the indicator was used. The original paper should be seen for details.

Mercury: According to Sloviter *et al.*,[96] Rupp's method (p. 370) gives high results, for iodine reacts slowly with formic acid. They reduce with hydrazine in alkaline solution, collect the mercury and determine it bromometrically. The procedure can be applied to organic compounds after a conventional decomposition with persulfate and sulfuric acid.

Procedure: To the solution of the mercury salt containing 50–100 mg. of mercury (after the decomposition) in a glass-stoppered flask, add 5 ml. of 20 per cent potassium iodide followed by 20 per cent sodium hydroxide solution until the liquid is alkaline with 5 ml. in excess. If a turbidity of mercuric oxide appears, add more iodide solution in 1 ml. portions until a clear solution is obtained. Rotate the flask while adding 10–15 ml. of 2 per cent hydrazine sulfate solution in a slow stream. Shake occasionally for about 10 minutes. Add 10 ml. of 5 per cent sodium bicarbonate solution and 5 ml. of 1 per cent magnesium sulfate heptahydrate solution while shaking the mixture. After about 5 minutes, add another 5 ml. of the magnesium solution, mix well, and allow to stand till the precipitate settles, leaving the supernatant liquid practically clear (10–15 minutes). Decant the solution through a retentive filter (e.g., Whatman No. 42), using a filter cone and light suction. Retain the greater part of the precipitate in the flask and wash thrice with water by decantation. Finally wash the filter thrice with water and transfer the paper with the precipitate to the flask.

Introduce about 25 ml. of water and then pipette in 25 ml. of 0.1N Koppeschaar's solution (2.8 g. of potassium bromate and 50 g. of potassium bromide per liter). Add rapidly 5 ml. of 6N sulfuric acid and immediately stopper the flask. Shake vigorously until the paper is disintegrated and no dark particles of mercury are visible. Immerse the flask in ice water and after 1–2 minutes add 10 ml. of 20 per cent potassium iodide solution. Shake well to absorb the bromine in the gaseous phase and titrate with 0.05*N* thiosulfate, using starch indicator. Shake well near the end of the titration to dislodge traces of iodine adhering to the filter paper. A blank with the bromate-bromide solution is run in presence of the filter paper.

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[94] W. Chorney and N. H. Furman, see *Analytical Chemistry of Manhattan Project*, C. J. Rodden, ed., McGraw-Hill, New York, 1950, p. 72.

[95] L. Erdey and L. Mázor, *Acta Chim. Acad. Sci. Hung.*, 3, 469 (1953).

[96] H. A. Sloviter, W. M. McNabb, and E. C. Wagner, *Ind. Eng. Chem., Anal. Ed.*, 13, 890 (1941).

Hydrogen Peroxide: The direct titration of hydrogen peroxide with bromate gives very good results, according to Szebellédy and Madis,[97] if a suitable hydrochloric acid concentration is used with manganous chloride as catalyst.

Procedure: Dissolve 1 g. of crystalline manganous chloride in 25 ml. of the approximately 0.1*N* peroxide solution. Add 25 ml. of 1*N* hydrochloric acid and titrate with 0.1*N* bromate until the solution becomes pale yellow about 0.5–1 ml. before the end-point. Heat the solution to about 40° C., wait until the oxygen development ceases, and then add 1 drop of bromate every 15–20 seconds until the solution turns permanently yellow. The titration must be done in a "white" flask and preferably with the use of a comparison solution containing 1 g. of manganous chloride in 50 ml. of 0.5*N* hydrochloric acid.

Nitrogen Compounds. *Hydrazine:* According to Kurtenacker and Wagner,[98] hydrazine can be directly titrated with bromate.

$$3N_2H_4 + 2HBrO_3 \longrightarrow 2HBr + 3N_2 + 6H_2O$$

Kolthoff[99] found that the method only gives good results if sufficient hydrochloric acid is present; otherwise, the results of Kurtenacker and Wagner were confirmed. In slightly acid solution N_3H and NH_3 were formed.[100]

Procedure: Add hydrochloric acid to the hydrazine solution to give a hydrochloric acid content of about 20 per cent. Add indigo as indicator and titrate with bromate to colorless.

Note: Strecker and Schartow[101] determine selenium in its compounds by reacting with a known amount of hydrazine. The precipitated selenium is filtered off and the residual hydrazine in the filtrate is titrated by the above method.

Szebellédy and Madis[102] titrate hydrazine with bromate, using phosphomolybdic acid as indicator. The method gives very exact results.

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[97] L. Szebellédy and W. Madis, *Z. anal. Chem.*, 109, 391 (1937).

[98] A. Kurtenacker and J. Wagner, *Z. anorg. Chem.*, 120, 261 (1921).

[99] I. M. Kolthoff, *J. Am. Chem. Soc.*, 46, 2011 (1924).

[100] Cf. A. W. Browne and F. F. Shetterley, *J. Am. Chem. Soc.*, **30**, 54 (1908).

[101] W. Strecker and L. Schartow, *Z. anal. Chem.*, 64, 218 (1924).

[102] L. Szebellédy and W. Madis, *Mikrochim. Acta*, 2, 57 (1937).

Procedure: Dilute the solution, which is about 0.1*N* in hydrazine, to about 40 ml. Dissolve 0.3 g. of powdered sodium molybdate in the liquid, add 10 ml. of 25 per cent phosphoric acid, and heat to 60–80°C. During the heating, the solution becomes dark blue. Titrate with 0.1*N* bromate solution until the color fades (about 0.2 ml. before the end-point). Then allow 30–40 seconds to elapse between each drop addition of titrant and titrate to colorless. Mineral acids interfere.

According to Kurtenacker and Kubina,[103] semicarbazide and phenylhydrazine can be determined in the same way as hydrazine.

Procedure: To 10–30 ml. of a 0.025*N* solution of the compound add 40 ml. of 1:1 hydrochloric acid and 2–3 g. of potassium bromide. Heat to 60°C. and titrate with 0.1*N* bromate solution in the presence of indigo as indicator.

Note: Methyl orange is not satisfactory because the bleaching is slow and the end-point is usually overshot.

Hydroxylamine: Bromate oxidizes hydroxylamine quantitatively to nitric acid:

$$BrO_3^- + NH_2OH \longrightarrow Br^- + H_2O + NO_3^- + H^+$$

Several investigators have applied the reaction to the determination of hydroxylamine.[104] An excess of bromate is added and the back-titration is done iodometrically.

Furman and Flagg[105] studied the reaction in order to apply it to the indirect determination of metals precipitated by oxime-type reagents. They preferred a standard arsenite solution for the back-titration owing to its being more stable than thiosulfate and to its not reacting with copper which might be present.

Procedure: To 25 ml. of hydroxylamine hydrochloride solution, add 50 ml. of 6*N* hydrochloric acid and sufficient 0.1*N* bromate solution to give about 10 ml. in excess. Rapidly stopper the flask. After 15 minutes, cool and add a measured excess of standard arsenite from a beaker. Rinse the beaker, add the washings to the flask, and titrate with 0.1*N* bromate in the presence of methyl orange as indicator.

Notes: (1) The method is suitable for up to 20 mg. of hydroxylamine.
(2) Copper after precipitation with salicylaldoxime or with α-benzoin oxime, and nickel after precipitation with dimethylglyoxime may be determined by this procedure.

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[103] A. Kurtenacker and H. Kubina, *Z. anal. Chem.*, **64**, 388 (1924).

[104] E. Rupp and H. Mäder, *Arch. Pharm.*, **251**, 295 (1913); A. Kurtenacker and J. Wagner, *Z. anorg. Chem.*, **120**, 261 (1921); A. Kurtenacker and R. Neusser, *ibid.*, **131**, 27, 36 (1923).

[105] N. H. Furman and J. F. Flagg, *Ind. Eng. Chem., Anal. Ed.*, **12**, 738 (1940).

Nitrite: Feit and Kubierschky[106] determined nitrite by oxidation with bromate; the bromine liberated was boiled out and an iodometric titration then used. Rupp and Lehmann[107] treated 10 ml. of solution (about 50 mg. of sodium nitrite) with an excess of bromate-bromide solution, added 10 ml. of dilute sulfuric acid, and after 30 minutes back-titrated iodometrically. Migray[108] carried out the oxidation in hydrochloric acid medium without the addition of bromide.

Procedure: To the test solution containing 40–200 mg. of nitrite add an excess of 0.1*N* bromate solution (20–50 ml.) and acidify with 5 ml. of concentrated hydrochloric acid. Immediately stopper the flask. Shake occasionally for 2–3 minutes, add 1–2 g. of potassium iodide, and titrate with thiosulfate solution.

Halides: Berg[109] developed a method in which iodide, bromide, and chloride can be titrated consecutively with potassium bromate in a medium of hydrocyanic acid.

$$BrO_3^- + 3I^- + 3CN^- + 6H^+ \longrightarrow 3ICN + Br^- + 3H_2O \qquad (1)$$

$$BrO_3^- + 2Br^- + 3CN^- + 6H^+ \longrightarrow 3BrCN + 3H_2O \qquad (2)$$

$$BrO_3^- + 2Cl^- + 3CN^- + 6H^+ \longrightarrow 2ClCN + BrCN + 3H_2O \qquad (3)$$

So long as iodide is present, only reaction (1) can occur because if any bromide does react to form bromine cyanide it is decomposed immediately by iodide.

$$I^- + BrCN \longrightarrow ICN + Br^-$$

The same holds when bromide is titrated in the presence of chloride.

Procedure. Iodide: To 60–70 ml. of solution add 5–10 ml. of *N* potassium cyanide solution and phosphoric, sulfuric, or hydrochloric acid to give a concentration of 30, 15, or 5–10 per cent, respectively. Add starch and titrate dropwise with 0.1*N* bromate until the color disappears. The iodine cyanide formed can, if preferred, be immediately titrated with thiosulfate.

Bromide: To 50–60 ml. of solution, add 10 ml. of *N* potassium cyanide and hydrochloric acid to give a concentration of 10–15 per cent and titrate with 0.1*N* bromate until the yellow bromine color disappears. Immediately add a mixture of 20 ml. of 10 per cent aniline hydrochloride and 10 ml. of 0.1*N* bromide. After 30–60 seconds, add 1 g. of potassium iodide and titrate with thiosulfate to the disappearance of the starch-iodine color.

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[106] W. Feit and K. Kubierschky, *Chem. Ztg.*, 15, 350 (1891); cf. A. Schwicker, *ibid.*, 845.

[107] E. Rupp and F. Lehmann, *Arch. Pharm.*, 249, 214 (1911).

[108] E. von Migray, *Chem. Ztg.*, 57, 48 (1933).

[109] R. Berg, *Z. anal. Chem.*, 69, 1, 342 (1926).

Notes: (1) The titration of bromide may follow on immediately after that of iodide.
(2) Chloride may be determined after the titration of bromide (p. 261).
(3) Matthes and Brause[110] applied Berg's method to the determination of iodine and iodide in tinctures.
(4) For the titration of iodide with potassium iodate see p. 471, and for the titration of chloride in the presence of bromide and iodide see Vol. II, p. 263.

Winkler[111] titrated small amounts of iodide in the presence of much bromide and hydrochloric acid and observed the end-point by the change of color of carbon tetrachloride. When concentrated hydrochloric acid and carbon tetrachloride are added to a solution containing small amounts of iodide and large amounts of bromide, and the mixture is titrated with a very dilute solution of potassium bromate, the solvent layer becomes rose-red on shaking. On further addition of bromate, the color deepens and then fades completely at the end-point while the aqueous layer becomes yellow.

$$\underset{\text{violet }(CCl_4)}{I^- + Br_2} \longrightarrow \underset{\substack{\text{faint yellow}\\ \text{(water)}}}{IBr + Br^-}$$

Procedure: Transfer 2–10 ml. of the test solution to a 50 ml. glass-stoppered Erlenmeyer flask and dilute if necessary with water to 10 ml. Dissolve 1 g. of potassium bromide in the solution, add 2 ml. of carbon tetrachloride, and acidify with 5 ml. of $12N$ hydrochloric acid. Titrate dropwise with $0.01N$ bromate solution until the red color of the solvent layer changes to colorless after shaking the stoppered flask thoroughly. One milliliter of $0.01N$ bromate corresponds to 0.6346 mg. of iodide.

Notes: (1) In this way 2–10 mg. of iodide can be titrated in the presence of 1 g. of sodium chloride or 1–2 g. of potassium bromide with an accuracy of 1 per cent. If less than 1 mg. of iodide is present in 1 g. of sodium chloride, the results are not satisfactory. For 0.1 mg. of iodine, it fails completely.
(2) If the salt contains a considerable amount of iodine, a sample containing 5–10 mg. of iodine is used. If more than 10 ml. of titrant is required, another 1 g. of potassium bromide should be added to the solution.

Phosphite and Hypophosphite: Rupp and Kroll[112] determined phosphite and hypophosphite by oxidizing for 1 hour in a sulfuric acid medium with twice the theoretical amount of bromate. The excess was titrated iodometrically.

Schwicker[113] was able to determine the two anions selectively. With bromate alone hypophosphite is oxidized completely, but phosphite only very slowly. With bromide present both ions are rapidly oxidized.

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[110] H. Matthes and G. Brause, *Pharm. Ztg.*, 72, 519, (1927).

[111] L. W. Winkler, *Z. anal. Chem.*, 87, 116 (1932); cf. *Z. angew. Chem.*, 28, 480 (1915).

[112] E. Rupp and Kroll, *Arch. Pharm.*, 249, 493 (1911).

[113] A. Schwicker, *Z. anal. Chem.*, 110, 161 (1937).

$$2BrO_3^- + 5PO_2^- + 2H^+ \longrightarrow 5PO_3^- + Br_2 + H_2O$$

$$2BrO_3^- + 5PO_3^- + 2H^+ \longrightarrow 5PO_4^- + Br_2 + H_2O$$

Procedure. Hypophosphite: To 10–20 ml. of approximately 0.025*M* hypophosphite solution add 5 ml. of 4*N* sulfuric acid and excess (25–30 ml.) of 0.1*N* potassium bromate. Heat just to boiling and, when bromine appears, set aside for 30 minutes to complete the oxidation. Boil off the bromine formed (pumice dust hastens the evolution). Cool and titrate the excess bromate with arsenite or thiosulfate in the usual way.

Phosphite and Hypophosphite: To the test solution, add 1–2 ml. of a solution of 2 g. of potassium bromide in 100 ml. of 0.1*N* potassium bromate and proceed as above.

Notes: (1) Schwicker[113] found that bromate in 1*N* hydrochloric acid solution could also be used to oxidize hypophosphite and phosphite to phosphate; bromine chloride is the active agent. The procedure is similar to the above method, but 90 minutes is required for complete oxidation.

(2) Deshmukh and Sant[114] determined red phosphorus by oxidizing with excess of standard bromate in approximately 0.5*N* sulfuric acid media.

$$6BrO_3^- + 6P + 6H_2O \longrightarrow 6PO_4^- + 3Br_2 + 12H^+$$

Procedure: Transfer the sample to a flask fitted with a reflux condenser and add an excess of standard bromate solution, 5–10 ml. of carbon tetrachloride or chloroform, 10 ml. of 4*N* sulfuric acid, and sufficient water to give a volume of about 100 ml. Reflux on a water bath for 1 hour or until all the red phosphorus disappears. Remove the condenser and boil gently to remove bromine from the organic solvent. Draw air through the solution to ensure complete removal of bromine. Cool to room temperature and back-titrate iodometrically.

Sulfur Compounds. *Thiocyanate:* The determination of thiocyanate has been studied by several investigators.[115] The reaction is as follows:

$$CNS^- + BrO_3^- + H_2O \longrightarrow SO_4^{2-} + Br^- + CN^- + 2H^+$$

Kurtenacker and Kubina[115] found the direct titration to be unsatisfactory because of the slow formation of bromine cyanide. The indicator (methyl orange or indigo) is destroyed before the reaction is complete. The iodometric back-titration is therefore to be preferred in this procedure.

Procedure:[115] Transfer 5–10 ml. of 0.2–0.3*N* thiocyanate to a 1 liter flask fitted with a stopper carrying a dropping funnel. Add 50 ml. of 0.2*N* potassium bromate, 10–15 ml. of 10 per cent potassium bromide solution, close the flask, and evacuate for 1–2 minutes at the pump. Add sufficient concentrated hydrochloric acid through the funnel to increase the volume by one third, taking care not to introduce air. Shake and set aside for 10–15 minutes (30 minutes for very dilute solutions). Add through the funnel 2-3 g. of potassium iodide dissolved in a little water without admitting any air. Shake, rinse the funnel, remove, and titrate with 0.1N thiosulfate in the presence of starch indicator.

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[114] G. S. Deshmukh and B. R. Sant, *Anal. Chem.*, **24**, 901 (1952).

[115] F. P. Treadwell and C. Mayr, *Z. anorg. Chem.*, **92**, 127 (1915); cf. A. Kurtenacker and H. Kubina, *Z. anal. Chem.*, **64**, 442 (1924).

Notes: (1) Kahane and Coupechoux[116] have described a similar procedure but back-titrate immediately. They apply this to the determination of reineckates after hydrolysis in alkaline solution.[117]

(2) Nakazono and Inoko[118] state that the direct titration is possible if the solution is 0.3–0.6N in hydrochloric acid and contains excess of potassium bromide.

According to Szebellédy and Madis,[119] direct titration with bromate is possible if gold chloride is used as indicator and ferric iron is also added.

Procedure: To 35 ml. of the neutral thiocyanate solution, add 3 g. of potassium bromide, 15 ml. of 2N hydrochloric acid, and 5 mg. of ferric ammonium sulfate. Titrate with 0.1N bromate solution until the intense red color disappears. Then add 1 ml. of 0.1 per cent gold chloride solution when the solution becomes pure yellow (which disappears in less than 30 seconds). Titrate dropwise with bromate until with the final drop the color remains stable and matches that of a comparison solution. Prepare the comparison solution with 35 ml. of water containing 3 g. of potassium bromide, 5 mg. of ferric alum, 15 ml. of 2N hydrochloric acid, 1 ml. of 0.1 per cent gold solution, and enough water to correspond to the final volume of test solution. The method is said to be very exact with 0.1N solutions.

Other Sulfur Compounds: Feit and Kubierschky[106] determined sulfide, sulfite, and thiosulfate by oxidation with a standard bromate solution and iodometric titration of the excess. Treadwell and Mayr[115] determined sulfide by the same procedure which they used for thiocyanate (p. 528). Mayr and Peyfuss[120] determined sulfite, thiosulfate, and dithionate by a similar method, but Hendrixson[121] was unable to obtain satisfactory results for sulfite by their procedure unless some iodide was added.

In general, bromate methods are inferior to iodometric methods for the titration of sulfur acids and are rarely used.

3. Determination of Organic Compounds. *Sulfur Compounds.*

Thiocarbamide: Under suitable conditions thiosemicarbazide is quantitatively oxidized by bromic acid according to the following equation:[122]

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[116] E. Kahane and R. Coupechoux, *Bull. soc. chim., France*, **1936**, 1589; cf. J. D'Ans and J. Mattner, *Angew. Chem.*, 63, 45 (1951).

[117] Cf. R. Montequi and J. G. Carreró, *Anales soc. españ. fís. y. quím. (Madrid)*, **31**, 242 (1933).

[118] T. Nakazono and S. Inoko, *Science Repts. Tôhoku. Imp. Univ. First Ser.*, **26**, 303 (1937).

[119] L. Szebellédy and W. Madis, *Z. anal. Chem.*, **114**, 343 (1938).

[120] C. Mayr and J. Peyfuss, *Z. anorg. Chem.*, **127**, 123 (1923); cf. C. Mayr and I. Szentpaly, *ibid.*, **131**, 203 (1923).

[121] W. S. Hendrixson, *J. Am. Chem. Soc.*, **47**, 1319, 2156 (1925); cf. R. C. Shaver and C. R. McCrosky, *Ind. Eng. Chem., Anal. Ed.*, **12**, 74 (1940).

$$3CS(NH_2)_2 + 4HBrO_3 + 3H_2O \longrightarrow 3CO(NH_2)_2 + 3H_2SO_4 + 4HBr$$

The titration is carried out in hydrochloric acid solution at 40–50°C. using gold trichloride as indicator; a comparison solution is used.

Mahr[123] considers that to avoid side reactions it is better to add iodide and to titrate with bromate to the blue starch end-point; the titration is done at about 35°C. in 5–6N sulfuric acid solution and 1 ml. of 1 per cent potassium iodide is added for every 20 ml. of solution. His method can be operated in the presence of ferric iron if phosphoric acid is added.

Dialkyl Sulfides: These compounds are oxidized according to the following reaction:[124]

$$R_2S \longrightarrow \underset{\text{sulfoxide}}{R_2SO} \longrightarrow \underset{\text{sulfone}}{R_2SO_2}$$

Because the second oxidation is slow, it is best to stay the reaction at the sulfoxide stage by titrating until just a slight excess of bromine is present. The results tend to be slightly high but, if the oxidation is carried out by adding an excess of oxidant and back-titrating, low results are obtained owing to incomplete oxidation to the sulfone. The method has been applied to diethyl, di-*n*-butyl, diisobutyl, and dibenzyl sulfides.

Procedure: Weigh about 0.002 mole of dialkyl sulfide into a 250 ml. Erlenmeyer flask and dissolve in 40 ml. of glacial acetic acid. Add 10 ml. of water (or less, if the sample precipitates) and 3 ml. of concentrated hydrochloric acid. Titrate with 0.1N bromate-bromide solution (2.78 g. of potassium bromate and 10 g. of potassium bromide per liter) until the first yellow color appears. Run a blank determination on the solvents; this also serves for the end-point correction.

Notes: (1) The blank is about 0.25 ml. The end-point is reproducible to 0.1 ml. so that, if the titers are large, the accuracy of the method is about 0.5 per cent.

(2) Mercaptans are also determined by the above procedure.

Alkyl Disulfides: These compounds may be determined by the procedure for dialkyl sulfides,[124]

$$RSSR + 5Br_2 + 4H_2O \longrightarrow 2RSO_2Br + 8HBr$$

[122] L. Szebellédy and W. Madis, *Z. anal. Chem.*, 114, 253 (1938).

[123] C. Mahr, *Z. anal. Chem.*, 117, 91 (1939).

[124] S. Siggia and R. L. Edsberg, *Anal. Chem.*, 20, 938 (1948).

but more acid is needed for complete reaction. The addition of 25 ml. of concentrated sulfuric acid is recommended for general purposes. Titration should be done at 30–50°C. Mixtures of alkyl disulfides and dialkyl sulfides may be analyzed by applying the above procedure and then determining the disulfide, after reduction, by the amperometric method of Kolthoff *et al.*[125]

The oxidation of acids of the type R—S—CH_2—COOH by the Siggia and Edsberg procedure has been studied but the method was not found to be satisfactory.[126] Thioacetals (mercaptals) may be determined if 25 ml. of glacial acetic acid and 20 ml. of concentrated hydrochloric acid are used, but thiolic esters react only slowly.[127]

Thiamine[128] and allyl isothiocyanate[129] have been determined by oxidation with excess of bromate-bromide solution. The original papers should be consulted for details.

Furfural: If an excess of the oxidant is present, 1 molecule of furfural in acid solution reacts with 2 molecules of bromine. The following procedure has been proposed for the determination of furfural[130] and has also been applied to the determination of pentoses and pentosans.[131]

Reagent: Bromate-bromide solution: 3 g. of potassium bromate and 50 g. of potassium bromide are dissolved in water and diluted to 1 liter.

Procedure: Dilute the furfural solution (distillate of the pentosan decomposition) to 500 ml. with 12 per cent hydrochloric acid. Transfer 25 ml. of the bromate-bromide mixture to a glass-stoppered flask and add 200 ml. of the furfural solution. Close the flask and set aside in the dark for 1 hour. Add 10 ml. of 10 per cent potassium iodide and titrate with 0.1*N* thiosulfate. One milliliter of 0.1*N* thiosulfate corresponds to 2.4 mg. of furfural.

Note: The results are about 2 per cent high. Other compounds which are oxidized by bromine interfere.

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[125] I. M. Kolthoff, D. R. May, P. Morgan, and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **18**, 442, (1946).

[126] B. Gauthier and J. Maillard, *Compt. rend.*, **236**, 1778 (1953).

[127] *Idem. ibid.*, 1890.

[128] P. Rózsa, *Magyar Kém. Folyóirat*, **61**, 122 (1955).

[129] G. Cavicchi, *Chem. Abstr.*, **30**, 473 (1948).

[130] W. J. Powell and H. J. Whittaker, *J. Soc. Chem. Ind.*, **43**, 35T (1924); cf. N. C. Pervier and R. A. Gortner, *Ind. Eng. Chem.*, **15**, 1255 (1923); H. A. Iddles and P. J. Robbins, *Ind. Eng. Chem., Anal. Ed.*, **5**, 55 (1933); O. C. Magistad, *ibid.*, 253.

[131] G. M. Kline and S. F. Acree, *Bur. Standards J. Research*, **8**, 25 (1932).

Hughes and Acree[132] described a method which yielded more accurate results. They carried out the reaction at a low temperature; under these conditions only 1 mole of bromine reacts with 1 mole of furfural.

Procedure: Transfer the sample (10–100 mg.) into 200 ml. of 3 per cent hydrochloric acid contained in a special flask fitted with two side arms (this is said not to be essential so long as bromine is not lost). Cool to 0–2°C. and add 25 ml. of 0.1*N* potassium bromate-bromide solution. Set aside for 3–10 minutes, add 10 ml. of 10 per cent potassium iodide, and shake vigorously to remove any bromine from the vapor phase. Rinse the stopper and titrate with 0.1*N* thiosulfate. One milliliter of 0.1*N* bromate corresponds to 0.0048 mole of furfural.

Notes: (1) Mixtures of methylfurfural and furfural may be determined by titrating aliquots at different times.[133] Methylfurfural reacts more rapidly than furfural.

(2) 5-Bromo-2-furoic acid can be determined by the above method if the reaction is allowed to proceed for 8–30 minutes at 21°C. Two moles of bromine react under these conditions.[134]

Oxalic Acid: In strong acid medium, oxalic acid is readily oxidized by bromate in the presence of manganous salt and mercuric sulfate.[135] The manganous salt is first oxidized to manganic, which reacts quickly with oxalic acid.

$$Mn_2O_3 + H_2C_2O_4 \longrightarrow 2MnO + 2CO_2 + H_2O$$

When phosphoric acid is present, a red manganic complex is formed at the end-point. The procedure can be applied to the determination of calcium and probably to other metals which form insoluble oxalates.

Procedure: Dilute the oxalate solution to about 30 ml., add 0.5 g. of manganous sulfate, 0.5 g. of mercuric oxide, 20 ml. of concentrated sulfuric acid, and 5 ml. of phosphoric acid. Titrate the hot solution with 0.1*N* bromate to a stable red color. One milliliter of 0.1*N* bromate corresponds to 4.502 mg. of oxalic acid.

Note: It is best to use a comparison solution prepared in exactly the same way as the test solution but without oxalate present and to add to this 0.1 ml. of 0.1*N* bromate. The test solution is titrated to this same color and 0.1 ml. is deducted from the titer.

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[132] E. E. Hughes and S. F. Acree, *Ind. Eng. Chem., Anal. Ed.*, **6**, 123 (1934); cf. R. Schiemann and W. Laube, *Z. anal. Chem.*, **136**, 26 (1952).

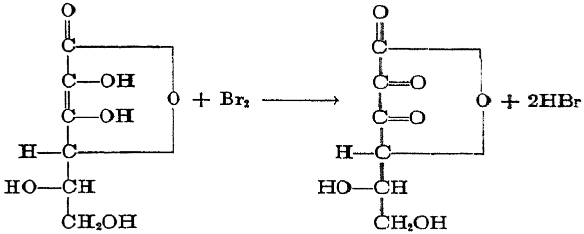
[133] E. E. Hughes and S. F. Acree, *Ind. Eng. Chem., Anal. Ed.*, **9**, 318 (1937).

[134] E. E. Hughes and S. F. Acree, *Ind. Eng. Chem., Anal. Ed.*, **6**, 292 (1934.)

[135] L. Szebellédy and W. Madis, *Z. anal. Chem.*, **114**, 347, 350 (1938); cf. W. Feit and K. Kubierschky, *Chem. Ztg.*, **15**, 350 (1890).

Formic Acid: Formic acid, formates,[136] and formaldehyde[137] have been determined by oxidation with bromate under suitable conditions. The original papers should be consulted for details.

Vitamin C (l-Ascorbic Acid): Schulek *et al.*[138] titrated vitamin C in the pure form or in medicinal preparations or injection liquids with potassium bromate.



Procedure: Dissolve an amount of sample containing 1–200 mg. of vitamin C in 10 ml. of water. Add 0.5 g. of potassium bromide, acidify with 5–10 ml. of 10 per cent hydrochloric acid, and add 1 drop of 0.2 per cent ethanolic solution of *p*-ethoxychrysoidine hydrochloride. Titrate with 0.01N (1–15 mg. of Vitamin C) or 0.1N (15–200 mg.) bromate until the red color just disappears. For titrations with 0.01N bromate, an indicator blank of 0.03 ml. is subtracted. One milliliter of 0.01N bromate corresponds to 0.8805 mg. of ascorbic acid.

Chloral Hydrate: Schwicker[139] determined chloral hydrate by titrating with bromate.

$$CCl_3CH(OH)_2 + BrO_3^- + OH^- \longrightarrow CCl_3CO_2^- + Br^- + 2H_2O$$

Procedure: To 30–40 ml. of 0.1N potassium bromate and 1 g. of potassium bromide, add 10 ml. of about 1 per cent chloral hydrate solution and 5 ml. of N hydrochloric acid. After 5 minutes, add 1 g. of powdered borax and set aside the closed flask for 15–20 minutes; shake occasionally during this time. Add an excess of 0.1N arsenious oxide solution and back-titrate with 0.1N bromate solution in the usual way. [Presumably acid is added. Authors.] One milliliter of 0.1N bromate corresponds to 8.27 mg. of chloral hydrate.

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[136] E. Rupp, *Arch. Pharm.*, **243**, 98 (1905); W. Poethke, *Pharm. Zentralhalle*, 86, 357 (1947).

[137] L. Spitzer, *Chem. Ztg.*, **57**, 224 (1933).

[138] E. Schulek, J. Kovács, and P. Rózsa, *Z. anal. Chem.*, **121**, 17 (1941).

[139] A. Schwicker, *Z. anal. Chem.*, **110**, 161 (1937).

Isonicotinyl Hydrazide: Haugas and Mitchell[140] preferred a bromometric to an iodometric titration for this determination. Lactose interferes with the latter and the results vary with the time of standing. The bromate oxidation yields constant results if 10 minutes or more are allowed for the reaction.

$$\mathrm{R{\cdot}CONHNH_2 + 2Br_2 + H_2O \longrightarrow R{\cdot}COOH + N_2 + 4HBr}$$

Procedure: Transfer 25 ml. of solution containing about 40 mg. of isoniazid to an iodine flask and add 25 ml. of $0.1N$ bromate-bromide mixture followed by 5 ml. of concentrated hydrochloric acid. Set aside for 10–15 minutes at 20–30°C. Add carefully 5 ml. of 20 per cent potassium iodide solution and titrate with $0.05N$ thiosulfate.

$$\text{Percentage of isoniazid} = \frac{(V - V_1) \times 1.715 \times f}{\text{sample wt. (g.)}}$$

where V = titer of bromate, V_1 = back-titration, f = factor of thiosulfate.

Various other organic substances have been determined by titration with bromate, e.g., allyl alcohol,[141] barbituric acid derivatives,[142] 3,3′-diethyl-2,4-dioxotetrahydropyridine (Persedon),[143] and undecylenic acid.[144] These methods are not very important; if required, further details should be sought in the original papers.

4. Bromate-Bromide Mixtures in Substitution Reactions. The use of a bromate-bromide solution for the bromine substitution reaction was introduced by Koppeschaar,[4] who applied it to the determination of phenol. The method has since been used widely and has been applied to many other compounds. Substitution reactions with bromine have already been discussed (Vol. I, p. 243). From the practical point of view, two methods are possible:

(*a*) The test solution is titrated with bromate-bromide mixtures until a permanent yellow color remains (or the solution is spotted on potassium iodide starch paper). In this way, for example, aniline can be converted to tribromoaniline.[145]

(*b*) A known amount of bromate-bromide solution is added to the test solution, which is then acidified and the excess of bromine is titrated iodometrically or by the arsenite method.

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[140] E. A. Haugas and B. W. Mitchell, *J. Pharm. and Pharmacol.*, 4, 687 (1952).

[141] E. Schulek and I. Bayer, *Acta Pharm. Intern.*, 1, 177 (1950).

[142] G. Schill, *Svensk Farm. Tidskr.*, 50, 385 (1946).

[143] F. Jaminet, *Chem. Abstr.*, 48, 1202 (1954).

[144] M. Masotti, *Atti accad. sci. Ferrara*, 30, 23 (1953).

[145] H. Reinhardt, *Chem. Ztg.*, 17, 413 (1893).

Methods (*a*) and (*b*) do not always give the same results, for many compounds, such as some naphthylamine- and naphtholsulfonic acids take up only 1 atom of bromine on direct titration; in presence of excess bromine, the substitution goes further; details of this are given by Vaubel.[146] In bromate substitution reactions, three sources of error are encountered.[147] These are oxidation and destruction of the molecule, precipitation of incompletely brominated products, and unwanted bromine substitution of certain groups such as —COOH, —SO_3H, —CHO.

The first difficulty is found especially with *o*- and *m*-toluidines, phenylenediamines, *o*- and *p*-aminophenols, *p*-phenetedine, and pyrocatechin. Usually, dark-colored solutions are obtained and the end-point is thus very difficult to see. If the reaction is carried out at less than 0°C., the error with toluidines, *p*-phenetedines, and *p*-aminophenol is avoided. The second complication is found especially with compounds substituted in the para position, such as *p*-nitroaniline and *p*-iodoaniline, and causes low results; it can be avoided by the addition of suitable solvent materials, preferably alcohol. The third difficulty leads to high results and can usually also be avoided by working at lower temperature (0°C.). Great caution must be observed with the hydroxybenzoic acids. Francis and Hill[147] gave the following table, where T_1 is the temperature below which the unwanted groups are not substituted at all and T_2 the temperature above which these substitutions take place quantitatively.

TABLE III

Substitution of Groups with Bromine

		T_2
o- and *p*-Hydroxybenzoic acid	−5	20
o- and *p*-Aminobenzoic acid	0	40
o- and *p*-Hydroxybenzaldehyde	10	40
o- and *p*-Aminobenzaldehyde	15	45
Sulfanilic acid	0	20

[146] W. Vaubel, *Die physikalischen und chemischen Methoden der quant. Bestimmung organischer Verbindungen*, 2, 166 (1902) (Berlin).

[147] A. W. Francis and A. J. Hill, *J. Am. Chem. Soc.*, 46, 2498 (1924).

TABLE IV

Bromometric Determination of Phenols and Amines according to Day and Taggart

Compound	Time of bromination (in min.)	Equiv. of Br per mole of compound
Phenol	5–30	6
p-Chlorophenol	30	4
o-Nitrophenol	30	4
m-Nitrophenol	5–30	6
p-Nitrophenol	5–30	4
2,4-Dinitrophenol	30	2
(Salicylic acid)	30	6
m-Hydroxybenzoic acid	15	6
Methyl salicylate	30	6
Phenyl salicylate	30	12
Acetylsalicylic acid	30	6
m-Cresol	1	6
Resorcinol	1	6
β-Naphthol	15–20	2
Thymol	15–20	4
Aniline	5–10	6
p-Chloroaniline	10	4
o-Nitroaniline	30	4
m-Nitroaniline	30	6
Acetanilide	5–10	6
Sulfanilic acid	30	6
Metanilic acid	5–15	6
Anthranilic acid	60	6
m-Aminobenzoic acid	10–15	6
m-Toluidine	5–10	6

When a compound contains two hydroxyl, two amino groups, or one of each, the meta compound yields the tribromo product; the *o*- and *p*-compounds, however, do not combine with any bromine. This is true with, for example, hydroquinone even at room temperature and with pyrocatechin, *p*-phenylenediamine, and *p*-aminophenol if the reaction is done at 0°C. to prevent oxidation. Thymol forms a dibromo compound and vanillin yields at 0°C. a monobromo derivative. Phloroglucinol gives a tribromo derivative, at least if the excess of bromine is back-titrated iodometrically.

Method of Day and Taggart: Day and Taggart[148] have critically examined the use of the Koppeschaar method for the determination of various organic compounds. In so far as the compounds are insoluble in water, phenols and sulfonic acids are dissolved in sodium hydroxide, while amines are dissolved in hydrochloric acid. An excess of bromate-bromide solution (about 100 per cent excess) is added to a suitable amount of the substance and 5 ml. of concentrated hydrochloric acid for each 100 ml. of solution is added. The mixture is shaken for 1 minute and after the given time of standing (see Table IV) the excess of bromine is back-titrated iodimetrically. Day and Taggart used 25 ml. of 0.2*N* bromate in about 0.7*N* potassium bromide solution; their results are summarized in Table IV.

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[148] A. R. Day and W. T. Taggart, *Ind. Eng. Chem.*, 20, 545 (1928).

Methyl salicylate, phenyl salicylate, and acetyl salicylate were saponified before the analysis. For the bromination of β-naphthol and thymol (cf. p. 542), 5 ml. of chloroform was also added, because otherwise the reaction proceeded irregularly; a blank determination was run under similar conditions. Acetanilide was hydrolyzed with acid before the titration (p. 543). For compounds which yield tribromoaniline by the bromination, such as sulfanilic acid or anthranilic acid, the reaction temperature should not be higher than 10–15°C.; otherwise oxidation also occurs.

p-Nitroaniline gave low results.

In the bromination of *p*-aminobenzoic acid, a mixture of insoluble dibromo derivatives and tribromoaniline was obtained; the consumption varied between 4 and 6 equivalents of bromine for the formula weight.

The determination of individual compounds by the bromine substitution method is described in the following pages.

Phenol: In 1871, Landolt[149] recognized that phenol can be readily brominated to tribromophenol. Koppeschaar[150] based on this reaction his well-known titration method for phenols, which even today is still generally used and gives satisfactory results.

$$C_6H_5OH + 3Br_2 \longrightarrow 3HBr + C_6H_2Br_3OH$$

Intrinsically, in a phenol solution with a large excess of bromine the substitution goes further to tribromophenolbromide, $C_6H_2Br_3OBr$, which however, is decomposed by potassium iodide to tribromophenol and a corresponding amount of iodine is liberated.

Procedure: To about 25 ml. of about 0.01 *M* phenol solution, add 25 ml. of 0.1*N* potassium bromate, 0.5 g. of potassium bromide, and 5–10 ml. of 4*N* hydrochloric or sulfuric acid. After 5–10 minutes, open the closed flask, add

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[149] H. Landolt, *Ber.*, 4, 770 (1871).

[150] W. F. Koppeschaar, *Z. anal. Chem.*, 15, 233 (1876).

1 g. of potassium iodide, shake well, and titrate with thiosulfate, using starch as indicator.

One milliliter of $0.1N$ bromate corresponds to 1.567 mg. of phenol.

Notes: (1) Redman *et al.*[151] investigated the effect of temperature, acidity, and time on the bromination. They recommended the addition of a 2 per cent excess of bromate-bromide mixture to a 0.5–$1N$ hydrochloric acid solution of phenol at 20–30°C. and back-titration after 1 minute; low temperatures retard the formation of tribromophenol.

(2) Schwicker[152] preferred to add an excess of standard arsenite solution after the reaction and to titrate finally with bromate solution in the presence of methyl orange as indicator.

(3) Bielenberg[153] examined several dyestuffs as indicators for the direct titration to the tribromophenol stage. The results appear to be unsatisfactory, the color change being masked by the tribromophenol. An improvement was effected by working in a strong acetic acid solution. but a suitable procedure could not be developed.

(4) Portner[154] determined phenol preservative in sera, vaccines, and protein solutions by first steam-distilling the phenol. Sodium formaldehydesulfoxylate yields hydrogen sulfide, but this may be overcome by distilling in the presence of lead acetate.

It is also possible to titrate the tribromophenolbromide which is formed when an excess of bromine is added.

$$C_6H_2Br_3OBr + 2KI \longrightarrow C_6H_2Br_3OK + I_2 + KBr$$

Procedure:[155] To 5–10 ml. of $0.1M$ phenol solution add 1 g. of sodium acetate and 20–40 ml. of saturated bromine water and shake thoroughly. Filter after 5–10 minutes and wash 5 times with 5 ml. of water. Transfer the precipitate to a glass-stoppered flask, add 5–10 ml. of N potassium iodide to the suspension, and set aside for 10 minutes with occasional shaking. Titrate with $0.1N$ thiosulfate. On milliliter of $0.1N$ thiosulfate corresponds to 4.7 mg. of phenol.

Notes: (1) This method gives results which are about 2 per cent low, and the method of Koppeschaar is more exact and simpler. However, when other bromine-consuming or bromine-substituting compounds are present, this method can be used advantageously.

(2) Salicylic acid forms tribromophenolbromide with an excess of bromine and can therefore be determined in a similar manner.

Cresols: Cresols are not brominated so readily as phenols. Danckwortt and Siebler[156] found that *m*-cresol could be brominated in 15 minutes but *o*- and *p*-cresols required up to 72 hours, depending on the amounts present.

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[151] L. V. Redman, A. J. Weith, and F. P. Brock, *Ind. Eng. Chem.*, **5**, 389 (1913).

[152] A. Schwicker, *Z. anal. Chem.*, **110**, 183 (1937).

[153] W. Bielenberg, *Ber.*, **75**, 686 (1942).

[154] P. E. Portner, *Anal. Chem.*, **22**, 570 (1950).

[155] I. M. Kolthoff, *Pharm. Weekblad*, **69**, 1147 (1932).

[156] P. W. Danckwortt and G. Siebler, *Arch. Pharm.*, **264**, 439 (1927); cf. K. K. Järvinen, *Z. anal. Chem.*, **71**, 108 (1927); **73**, 446 (1928).

Kolthoff found that freshly prepared *m*-cresol takes up 3 bromine atoms and so can be determined in the same way as phenol.[157] The *m*-cresol, however, decomposes very rapidly on standing and even after fractionation at the correct boiling point always consumes less than 3 atoms of bromine.

p-Cresol and *o*-cresol seem to be able to substitute 2 atoms of bromine. Working with a Kahlbaum preparation, Kolthoff always found that slightly more than 2 atoms are absorbed. The amount of bromine taken up is strongly dependent on the bromine and acid concentration and on the time of the reaction.[158] Beukema-Goudsmit[157] could not obtain good results with *o*- and *p*-cresol. A method for the determination of *o*-cresol in which the reaction is stayed at the dibromo stage has been described by Aichenegg and Haynes.[159]

Procedure: Dissolve 0.5–0.8 g. of *o*-cresol in 10–20 ml. of N sodium hydroxide and dilute to 250 ml. with water. Transfer 25 ml. to a 250 ml. iodine flask and add 25 ml. of 1:4 hydrochloric acid. Adjust the temperature to 20–25°C. and add $0.1N$ potassium bromate-bromide solution until a yellow color is obtained. Add 2–4 ml. in excess. Complete this operation in not more than 15 seconds. Stopper the flask, shake for 30 ± 5 seconds, add 10 ml. of 10 per cent potassium iodide, and titrate after 3 minutes with $0.1N$ thiosulfate in the presence of starch indicator. One milliliter of $0.1N$ bromate corresponds to 2.704 mg. of *o*-cresol.

Notes: (1) The method is also applicable to the determination of 4-chloro-2-methylphenol and 2-methylphenoxyacetic acid, 1 mole of bromine being taken up. Take 1.0–1.5 g. of the former or 1.5–2.0 g. of the latter and add 20 ml. of ethanol or methanol to a 25 ml. aliquot. Add 5 ml. of concentrated hydrochloric acid and cool to 20–25°C. Proceed as before but add 60 ml. of water before the starch indicator.

(2) Immiscible solvents may cause low results, but the addition of methanol or ethanol (40–60 per cent v/v in the solution made $1N$ in hydrochloric acid) overcomes this effect.

(3) Chlorinated 2-methylphenoxyacetic acids do not react.

Phenol Derivatives: Sprung[160] found that the following phenols give stoichiometric results in the bromination: phenol, *m*-cresol, 3,5-xylenol, *m*-ethylphenol (each consumes 6 equivalents of bromine per mole); *p-tert*-butylphenol, *p-tert*-amylphenol, thymol, *p*-bromophenol (each consumes 4 equivalents of bromine per mole); 2,4-dichlorophenol (2 equivalents) and 2,2-(*p,p'*-dihydroxydiphenyl)-propane (8 equivalents). Quite generally, phenols which contain substituents in the meta position react with acid bromate-bromide solution to give quantitative substitution at the ortho and para positions. Phenols which contain primary alkyl groups in the ortho or para positions give results which may be 10 to 150 per cent, depending on the nature of the substituents. Certain phenols having primary alkyl substituents in the para position (*p*-ethylphenol) can be determined with reasonable accuracy and fair precision at 5°C. if the time of bromination is limited to 2–3 minutes.

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[157] Cf. M. Beukema-Goudsmit, *Pharm. Weekblad*, 71, 380 (1934).

[158] Cf. R. D. Scott, *Ind. Eng. Chem., Anal. Ed.*, 3, 67 (1931); J. A. Shaw, *ibid.*, 273.

[159] P. Aichenegg and H. G. Haynes, *J. Appl. Chem. (London)*, 4, 137 (1954).

[160] M. M. Sprung, *Ind. Eng. Chem., Anal. Ed.*, 13, 35 (1941).

Procedure: Dissolve 2 g. of sample in 50 ml. of water and 10–15 ml. of 10 per cent potassium hydroxide. Transfer to a volumetric flask and dilute to 250 ml. Place a 10 ml. aliquot in a 250 ml. iodine flask and add 25 ml. of 0.1*N* potassium bromate, 10 ml. of 2*N* potassium bromide, 50 ml. of water, and 2–3 ml. of concentrated hydrochloric acid. Stopper and fill the cup of the flask with water. Shake occasionally over a period of 10 minutes. Add carefully 1 ml. of 10 per cent potassium iodide and set aside for 10 minutes. Rinse the cup and walls of the flask with water and titrate the liberated iodine with 0.1*N* thiosulfate. A blank determination should be carried out.

Note: Francis and Hill[161] state that overbromination can be avoided in the above method by adding only a slight excess of bromine and restricting the time of reaction.

Ruderman[162] studied the effect of time of reaction, temperature, and excess of bromine present. He applied a modified Koppeschaar procedure[151] and found that overbromination of *o*-cresol increases with increase of these three factors; *o*-cresol overbrominates more readily than *p*-cresol. Sprung considered that bromination occurred in alkyl groups ortho or para to the phenolic hydroxy group; Ruderman suggested as an alternative explanation that methylene quinones are formed, and consume additional bromine. No direct evidence is available to support either theory.

Ruderman also studied the bromination of many other phenolic derivatives. He concluded that no universal bromination procedure can be used with confidence for all types of such compounds. But a large number may be determined quite accurately if it is known which brominate normally and which abnormally; the procedure may then be modified accordingly.

Spliethoff and Hart[163] analyzed several alkylated phenol mixtures by a similar procedure. They confirmed that reproducible results can only be obtained by careful control of the factors which affect bromination.

The most recent systematic study is due to Erichsen and Rudolphi.[164] They divide phenolic compound into three classes.

(*a*) Phenols which form tribromo derivatives: phenol, *m*-cresol, 3,5-dimethylphenol, 3-methyl-5-ethylphenol, and 3,5-diethylphenol. Other phenols with alkyl groups substituted in the meta positions can certainly be assumed to react in the same way. Bromination is rapid and should be allowed to proceed for not less than 1 minute at 20°C. In some cases a flocculent precipitate of the dibromoderivative separates and the complete bromination of the occluded material is slow; 3,5-dimethylphenol should be allowed to react for at least 3 minutes. To avoid the interference of tribromophenolbromide or its analogues with the iodometric end-point, it is recommended that some milliliters of chloroform be added near the end-point of the titration, which is then completed with strong shaking. A rise in temperature of 10° C. doubles the bromination rate.

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[161] A. W. Francis and A. J. Hill, *Ind. Eng. Chem., Anal. Ed.*, **13**, 357 (1941).

[162] I. W. Ruderman, *Ind. Eng. Chem., Anal. Ed.*, **18**, 753 (1946).

[163] W. L. Spliethoff and H. Hart, *Anal. Chem.*, **27**, 1492 (1955).

[164] L. V. Erichsen and N. Rudolphi, *Erdöl u. Kohle*, **8**, 16 (1955).

(*b*) Phenols which form dibromo derivatives: *o*-cresol, 2,3-dimethylphenol, and 2,5-dimethylphenol form the dibromo derivatives in approximately 1 minute. These compounds can readily be determined if the iodide is added whenever the first yellow color of excess bromine appears.

(*c*) Phenols with undefined bromination processes: These are mainly derivatives with the alkyl groups in the para position such as *p*-cresol, *p*-ethylphenol, 2,4-, 3,4-, and 2,6-dimethylphenol and 2,3,5- and 2,4,5-trimethylphenol. The reaction appears to be very complex and oxidation and addition may occur as well as substitution. The bromination of these compounds is therefore unsuitable for analytical purposes.

Procedure: Transfer the aqueous solution of the phenol to the flask described on p. 29 and add an excess of 0.1*N* bromate-bromide solution. Place 5–10 ml. of 10 per cent potassium iodide solution in the bulbs of the outlet tube, acidify the solution in the flask with 20–25 per cent sulfuric acid, and immediately insert the moistened stopper. After the bromination period, suck out a little air from the flask and allow the iodide solution to run in. (No loss of bromine is possible since the air sucked out bubbles through the iodide solution.) Rinse the outlet tube into the flask and titrate with 0.1*N* thiosulfate in the usual way.

Notes: (1) The results are reproducible to 0.3 per cent; 2 mg. of phenol in 50 ml. of water can be determined with an accuracy of ± 5 per cent.

(2) The analysis of binary phenol mixtures was also studied. Erichsen and Rudolphi recommended the use of calibration curves prepared under the conditions given above.

2,4-Dinitrophenol: Johnson *et al.*[165] tried to determine 2,4-dinitrophenol in the presence of picric acid and found that the latter consumes bromine and a displacement of the nitro group may occur. They noted that when overconsumption of bromine occurred, nitrous acid was always to be found in the solution; this affected the end-point of the iodometric titration. They studied the effects of various factors which influence the bromination of nitro compounds and as a result were able to choose conditions for the determination under which interference by picric acid was reduced to insignificant amounts.

[165] L. D. Johnson, W. M. McNabb, and E. C. Wagner, *Anal. Chem.*, 27, 1494 (1955).

Procedure (for picric acid and 2,4-dinitrophenol in admixture): Transfer the sample (containing 30–300 mg. of 2,4-dinitrophenol) to a 500 ml. iodine flask and dissolve in a slight excess of 0.1*N* sodium hydroxide. Add a slight excess of 0.1*N* acid and complete the titration with the 0.1*N* alkali in the presence of phenolphthalein as indicator. For reproducibility and certainty the titrations were taken to a rather deep color (a similar method was used for the standardization of the alkali). To the titrated, nearly neutral solution, add 25 ml. of 0.1*N* bromate-bromide solution (about 100 per cent excess) and, without shaking, 5 ml. of concentrated hydrochloric acid and immediately stopper the flask. Set in the dark for 30 minutes at 20–25 °C. Add 5 ml. of 40 per cent potassium iodide solution and titrate with 0.1*N* thiosulfate, adding 5 ml. of 1 per cent starch near the end-point.

Notes: (1) The amount of picric acid present is calculated from the total amount of phenols determined alkalimetrically.

(2) The alkali is standardized against 99.95 per cent picric acid.

Phenolsulfonic Acid: Depending on the reaction conditions, phenolsulfonic acid can take up 2, 3, or more atoms of bromine. Grant[166] studied this substitution thoroughly and gave methods for the substitution by 2 or 3 atoms. However, the results are strongly dependent on the acidity of the solution, the excess of bromine, and the time of reaction, so that the procedure cannot be recommended for general use. Sager *et al.*[167] applied the Hughes-Acree method for furfural (p. 532) at 0°C. Under these conditions 2 moles of bromine react in 5–10 minutes with 1 mole of potassium *p*-phenolsulfonate to form 2,6-dibromophenol-4-sulfonate.

Resorcinol, $C_6H_4(OH)_2$: The Koppeschaar method is suitable for the determination of resorcinol, which gives a tribromo substitution product (1 ml. of 0.1*N* bromate corresponds to 1.833 mg. of resorcinol) but not for the titration of other di- or trivalent phenols.

Resacetophenol has been determined to within ±5 per cent by making use of an extrapolation method.[168]

Thymol: Hart[169] determined thymol by the usual back-titration procedure and by direct titration with methyl orange as indicator (cf. p. 537). He considered the latter procedure the better one, but both gave results within 1 per cent.

β-Naphthol: The accuracy of the following method is claimed to be 0.1 per cent.[170]

Procedure: Dissolve 2 g. of β-naphthol in 25 ml. of *N* sodium hydroxide and dilute with water to 250 ml. in a graduated flask. Add 20 ml. of this solution to 100 ml. of water in an iodine flask and add 50 ml. of 0.1*N* bromate containing 5 g. of potassium bromide per liter. Add 2 drops of methyl orange solution and 15 ml. of *N* hydrochloric acid. Stopper the flask and set aside until the pink color disappears (about 15 minutes). Immediately add 10 ml. of 25 per cent potassium iodide and 10 ml. of hydrochloric acid and titrate with 0.1*N* thiosulfate solution.

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[166] E. H. Grant, *J. Assoc. Offic. Agr. Chemists*, 14, 351 (1931).

[167] E. E. Sager, M. R. Schooley and S. F. Acree, *J. Research Natl. Bur. Standards*, 31, 197 (1943).

[168] K. Neelakantan and G. Viswanath, *Proc. Indian Acad. Sci.*, 35A, 72 (1952).

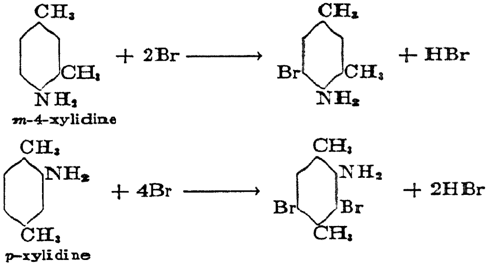
[169] L. Hart, *J. Assoc. Offic. Agr. Chemists*, 12, 296 (1929).

[170] L. C. Weiss, *J. Assoc. Offic. Agr. Chemists*, 25, 896 (1942).

Aniline: Aniline can be titrated in exactly the same way as phenol; it yields an analogous tribromoaniline.[145] Kolthoff has found that the procedure is very exact even at high dilutions. If in the back-titration with thiosulfate the tribromoaniline appears to adsorb iodine(which is recognized by the darkening of the white precipitate), a little alcohol or chloroform is added near the end of the titration. Callan and Henderson[171] recommended direct titration with bromate-bromide mixture; starch-iodine paper was used as external indicator. The procedure was also applied to several derivatives. The direct bromometric titration of aniline is also possible (p. 565).

The method can also serve for the determination of acetanilide. A weighed amount of acetanilide is decomposed by boiling for 15 minutes in 4*N* hydrochloric acid solution to aniline and acetic acid, and the aniline is then determined as described.

Xylidine: Fedorow and Spryskow[172] examined the titrimetric determination of xylidine isomers with bromate-bromide. It is best to titrate an alcoholic solution of xylidine which is about 2*N* in hydrochloric acid with aqueous bromate-bromide solution (19–20 g. of potassium bromate and 28–30 g. of potassium bromide per liter) at 0–5°C. *m*-4 and *m*-2 Isomers with free ortho and para positions for amino groups form monobromoxylidine (1 mole requires 2 equivalents of bromine), whereas an *o*-4 isomer with two free ortho positions or *o*-3 and *p*-isomer with two free ortho and para positions for amino groups form dibromoxylidine.



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[171] T. Callan and J. A. R. Henderson, *J. Soc. Chem. Ind. (London)*, **41**, 161T (1922).

[172] B. P. Fedorow and A. A. Spryskow, *Z. anal. Chem.*, **105**, 412 (1936).

Salicylic Acid: Salicylic acid acts toward bromine somewhat similarly to phenol. According to Freyer,[173] it forms with an excess of bromine tribromophenolbromide, $C_6H_2Br_3OBr$ (or quinoid, $C_6H_2OBr_4$), which reacts with potassium iodide to give tribromophenol and free iodine.

One mole of salicylic acid consumes 6 equivalents of bromine. Freyer used for the titration an excess of about 100 per cent of bromine. Fresenius and Grünhut[174] recommended the following method.

Procedure: Dilute the bromate-bromide mixture (sufficient to give 75–80 per cent in excess) to 300 ml. with water and add 30 ml. of 20 per cent hydrochloric acid. Run in the test solution containing about 1 per cent of salicylic acid; a white precipitate forms. Close the flask and after 5 minutes of occasional shaking add 30–40 ml. of 10 per cent potassium iodide and titrate the liberated iodine with thiosulfate, using starch as indicator.

Kolthoff[175] found that the above method gave good results so long as the acidity was not too great. Day and Taggart, however, claimed that good results were obtained at higher acidities.

Procedure: To 25 ml. of approximately $0.01M$ salicylic acid solution in a glass-stoppered flask add 25 ml. of $0.1N$ bromate solution, 0.5–1 g. of potassium bromide and a maximum of 5 ml. of $4N$ hydrochloric acid. Set aside for 5–10 minutes, add 5 ml. of N potassium iodide, and titrate after 5 minutes with $0.1N$ thiosulfate. Near the end of the titration, add starch as indicator and shake vigorously so that all the adsorbed iodine returns into solution. Sometimes the precipitate at the end-point is not pure white but slightly blue in color and cannot be bleached by a large amount of thiosulfate; this phenomenon is not, however, due to iodine-starch. One milliliter of $0.1N$ bromate corresponds to 2.30 mg. of salicylic acid.

Notes: (1) The method is also suitable to the titration of very small amounts of salicylic acid if the acid concentration is correct (5 ml. of $4N$ hydrochloric acid per 50 ml. of solution). Kolthoff determined 2–4 mg. of the organic acid with an accuracy of 1 per cent.

(2) Kolthoff[176] established that the first two atoms of bromine are absorbed without addition. On further addition of bromine, the dibromosalicylic acid splits off carboxylic acid to form tribromophenol. This is then converted by excess of bromine to tribromophenolbromide, which is reduced by potassium iodide to tribromophenol. According to Beukema-Goudsmit,[177] low results can be obtained in the presence of large amounts of salicylic acid because dibromosalicylic acid is formed which is but slightly soluble and is only slowly converted to tribromo-

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[173] F. Freyer, *Chem. Ztg.*, **20**, 820 (1896); see also J. Houben, ed., *Die Methoden der organischen Chemie*, Vol. III, Thieme, Leipzig, 1923, p. 857.

[174] W. Fresenius and L. Grünhut, *Z. anal. Chem.*, **38**, 298 (1899).

[175] I. M. Kolthoff, *Pharm. Weekblad*, **58**, 699 (1921).

[176] I. M. Kolthoff, *Pharm. Weekblad*, **69**, 1159 (1932).

[177] M. Beukema-Goudsmit, *Pharm. Weekblad*, **71**, 380 (1934).

phenol. From her results, the salicylic acid concentration before the addition of bromate, etc., should be less than 0.003*M*.

(3) *p*-Hydroxyphenylpropionic acid may be determined as follows.[178] Dissolve 90–100 mg. of the acid by heating in 10 ml. of water, cool, add 40 ml. of 0.1*N* bromate and 10 ml. of 20 per cent bromide. Stopper the vessel and place in an ice bath for 10 minutes. Add rapidly 15 ml. of ice-cold 1:3 sulfuric acid, stopper the vessel, and shake vigorously. After 3 minutes add 25 ml. of 20 per cent potassium iodide. Titrate with 0.1*N* thiosulfate.

Aminobenzoic Acids and Derivatives: Valencien and Deshusses[179] found that bromination is a convenient means of estimating esters of *o*- and *p*-aminobenzoic acid. Wells[180] made a critical study of the method with a large number of compounds and used both direct and indirect titrations. In many cases, the direct titration has advantages because it is very simple and because various bromination products react with iodine to form colored compounds. This compound formation may be prevented by the addition of a mixture of mercuric chloride and potassium iodide instead of potassium iodide in the back-titration of the excess of bromine. (Wells did not use the arsenite method for the back-titration.) The original papers should be consulted for details.

Sulfanilamide and Derivatives: Nielsen and Wolffbrandt[181] give the following method for the determination of sulfanilamide, sulfapyridine, sulfathiazole, and *N*-(*p*-aminobenzenesulfonyl)-acetamide (albucid).

Procedure: Dissolve 300 mg. of the drug in 5 ml. of dilute hydrochloric acid and dilute to 100 ml. with water. Transfer a 20 ml. aliquot to a 500 ml. iodine flask and neutralize to phenolphthalein with *N* sodium hydroxide. Add 30 ml. of water, 20 ml. of 0.1*N* potassium bromate, 10 g. of potassium bromide, and 5 ml. of concentrated hydrochloric acid. Moisten the stopper with 10 per cent potassium iodide solution and stopper the flask. After the proper bromination time, add 10 ml. of 10 per cent potassium iodide solution and 250 ml. of water and titrate the liberated iodine with standard thiosulfate solution. Bromination times: sulfanilamide, albucid, 5 minutes; sulfapyridine, 10 seconds (longer gives high results); sulfathiazole, 2 hours. One milliliter of 0.1*N* bromate corresponds to 4.302 mg. sulfanilamide, 5.352 mg. albucid, 6.228 mg. sulfapyridine, and 5.352 mg. sulfathiazole. The sulfathiazole forms a tribromo derivative and uses 6 atoms of bromine, the others require 4 atoms of bromine.

[178] A. K. Ruzhentseva and N. S. Goryacheva, *Aptechnoe Delo*, **3**, No. 5, 7 (1954).

[179] C. Valencien and J. Deshusses, *Mitt. Lebensm. Hyg.*, **30**, 246 (1939).

[180] E. H. Wells, *J. Assoc. Offic. Agr. Chemists*, **25**, 537 (1942); cf. *ibid.*, **24**, 736 (1941).

[181] I. S. Nielsen and C. G. Wolffbrandt, *Dansk Tidsskr. Farm.*, **14**, 113 (1940).

Note: Wojahn[182] carried out the bromination with excess of bromate in a solution containing 5–10 per cent hydrochloric or sulfuric acid, 50 per cent acetic acid, and 1 g. of potassium bromide. He found the following bromination times to be satisfactory; 6-sulfanilamide-2,4-dimethylpyrimidine, sulfaethylthiadiazole, sulfaguanidine, sulfaurea, *p*-aminobenzenesulfonamide, sulfacetamide, Uliron, Neouliron, 2 minutes; diaminodiphenyl sulfone, Tibatin, sulfathiazole, sulfamethylthiazole, sulfapyrimidine, sulfa-4-methylpyrimidine, 5 minutes; Irgafen, 20 minutes; Irgamide, 60 minutes; sulfapyridine, 10 seconds.

Antipyrine: Schulek and Kovács[183] give the following method in which caffeinebenzoate or citrate, phenacetin, acetylsalicylic acid, and glycerol do not interfere. Care should be taken because antipyrine may be overbrominated in too acid solutions.

Procedure: To 10–15 ml. of solution containing 1–200 mg. of antipyrine, add hydrochloric acid to give a concentration of 5 per cent, 0.5–1 g. of potassium bromide, and 1 drop of 0.2 per cent *p*-ethoxychrysoidine solution (p. 505). Titrate with 0.01 or 0.1*N* bromate solution until the color is discharged. One milliliter of 0.1*N* bromate corresponds to 9.406 mg. of antipyrine.

***p*-Aminobenzenesulfonamide and Derivatives:** At a suitable acidity and if a 10–30 per cent excess of bromine is present, *p*-aminobenzenesulfonamide yields a dibromo substitution product.[184]

$$NH_2C_6H_4SO_2NH_2 + 2Br_2 \longrightarrow NH_2C_6H_2Br_2SO_2NH_2 + 2HBr$$

Schulek and Rózsa[185] examined the bromination reactions of several aminobenzenesulfonamide derivatives. They recommended three procedures and indicated which should be used for a particular compound (Table V).

When the hydrogen atom of the sulfonamide group is replaced by a benzosulfodimethylamide group in the para position, e.g., compound 2, Table V, the bromine ratio remains the same without previous acid hydrolysis; the same is true for compound 6. If the substituted group, benzosulfomonomethylamide, is in the para position (compound 3), bromination is only successful if the slight excess of bromine is back-titrated without waiting or, if a large excess is used, the bromination is done at 0°C.; here a progressive bromination must be reckoned with, which is often found with various aromatic compounds. If a benzosulfonamide group is substituted in the para position (compound 5), the ratio is the same as for compound 3. In compound 7, where the pyridine group is present, the bromination is only successful if an indicator is used which shows the end of the first bromination step at room temperature. With an excess of bromine, the bromination must be done at 0°C.; in this case the bromination goes to the second step (tribromination with a bromine atom in the pyridine ring). Thus the equivalent weight is one sixth of the molecular weight.

Similar ratios are found with the thiazole ring (compound 8), but here the tribromo compound is formed at once with 1 bromine atom in the thiazole ring.

With the *p*-aminobenzosulfonamide group substituted on the amino group

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[182] H. Wojahn, *Süddeut. Apoth. Ztg.*, **88**, 395 (1948); cf. *Arch. Pharm.*, **281**, 289 (1943).

[183] E. Schulek and J. Kovács, *Ber. ung. pharm. Ges.*, 16, 344 (1940); *Chem. Abstr.*, **34**, 7063 (1940).

[184] E. Schulek and I. Boldizsár, *Z. anal. Chem.*, **108**, 396 (1937).

[185] E. Schulek and P. Rózsa, *Z. anal. Chem.*, **122**, 96 (1941).

TABLE V

Bromination of Aminobenzenesulfonamide Derivatives

Compound[a]	Trade name	No. of bromine atoms substituted Method 1	Method 2	Method 3
1. *p*-Aminobenzenesulfonamide	Prontosil, etc.	2	2	3
2. 4(4′-A)benzenesulfondimethylamide	Uliron	2	2	6
3. 4(4′-A)benzenesulfonmethylamide	Neouliron	2	2	6
4. 4(4′-acetyl A)benzenesulfonamide	Neosanamide I	2	2	6
5. 4(4′-A)benzenesulfonamide	Neosanamide II	2	2	6
6. *p*-Aminobenzenesulfonacetylamide	Albucid	2	2	3
7. *p*-Aminobenzenesulfo-α-pyridinamide	Sulfapyridine	2	3	3
8. 2(*p*-A)thiazole	Sulfazole	3	3	—
9. *p*-Succinylaminobenzenesulfonamide	Succinyl-Ambeside	2	2	3
10. *p*-Succinyl-A-*p*-phenylazo-α,α′-diaminopyridine	Ritosept	2	2	—
11. *p*-Diacetyldioxydiphenylsulfone	Gonophen	4	4	—

[a] A represents the aminobenzenesulfonamino group.

(compounds 4 and 9), bromination is only possible after hydrolysis by boiling with hydrochloric acid (compounds 4 and 9) or with sodium hydroxide (compound 4).

After strong hydrolysis with sulfuric acid, compounds 1–7 and 9 give sulfanilic acid and in the bromination of these products by method 3, tribromoaniline is formed with splitting out of sulfuric acid.

Procedure 1: Transfer 0.5–1 meq. of the compound to a 500 ml. flask fitted with a ground stopper and dissolve in 2–3 ml. of 10 per cent sodium hydroxide solution. Add 200 ml. of water, 25 ml. of 38 per cent hydrochloric acid, and 1 g. of potassium bromide. Titrate with 0.1*N* bromate, shaking well, until a permanent yellow color of bromine appears. Add 1 g. of potassium iodide, stopper the flask, and titrate after 5 minutes with 0.1*N* thiosulfate in the presence of starch indicator.

Notes: (1) With compounds 4 and 9 (Table V) first hydrolyze the acetyl or succinyl group by boiling under reflux for 30 minutes with 10 per cent hydrochloric acid.

(2) With compounds 3 and 5, it is necessary to back-titrate immediately.

(3) Overbromination can occur with compound 7: hence titrate with bromate in the presence of 2–3 drops of 0.2 per cent ethanolic *p*-ethoxychrysoidine hydrochloride until the color disappears; add more indicator to check that the end-point has been reached. Alternatively dissolve in 50 ml. of 10 per cent hydrochloric acid, add 1 g. of potassium bromide, 1–2 drops of indicator, and titrate with bromate solution to colorless. Dilute to 150 ml., add 1 g. of potassium iodide, and titrate with 0.1*N* thiosulfate solution.

(4) With compound 10, extract the azo dye with chloroform from alkaline solution, then determine as above after hydrolysis (note 1).

(5) With compound 11, hydrolyze by refluxing with 70 per cent sulfuric acid for 10 minutes, then determine as above.

Procedure 2: Transfer the compound to a bromination flask (Fig. 5, p. 29), dissolve as before, add 30 ml. of water, a measured (10–40 per cent) excess of bromate, 1 g. of potassium bromide, and (rapidly) 10 ml. of 38 per cent hydrochloric acid. Close the flask. After 5 minutes, cool, draw in 10 ml. of 5 per cent potassium iodide, shake, dilute to 350 ml. with water, and titrate with 0.1*N* thiosulfate.

Note: Compounds 3 and 7 must be brominated at 0°C. Notes (1), (4), and (5) of procedure 1 also apply to procedure 2. The method is only accurate to 2–3 per cent for compound 5.

Procedure 3: Hydrolyze with 70 per cent sulfuric acid. Determine the undistilled products of decomposition, i.e., *p*-sulfanilic acid or, for compound 7, α-aminopyridine, by procedure 2, after transferring the residue to a bromination flask. Allow the bromination of compounds 3 and 5 to proceed for 1 hour.

Notes: (1) 2(*p*-Aminobenzenesulfonamino) - 4 - methylthiazole, *p* - benzylaminobenzenesulfonamide sodium sulfonate, 2,4-diaminoazobenzene-4′-sulfonamide, and 4-sulfonamidophenylazo-7-acetylamino-1-hydroxynaphthalene-3,6-disulfonic acid (sodium salt) could not be analyzed by any of the three procedures.

(2) Schulek and Rózsa[185] also describe the general properties of these compounds and give methods for their separation from pharmaceutical materials.

Dialkyl Phenylureas: These compounds (centralites) are used as stabilizers in smokeless powders. They react with bromine

$$OC{=}(N\cdot C_2H_5\cdot C_6H_5) + 2Br_2 \longrightarrow 2HBr + OC{=}(NC_2H_5C_6H_4Br)_2$$

and several determinations involving this reaction have been described.

Procedure:[186] Extract 5 g. of sample with ether for 24 hours. Evaporate the extract to constant weight and transfer the liquid residue to a 250 ml. volumetric flask with 50 ml. of ethanol. Add 25 ml. of bromate–bromide solution, cool to 25°C., and add 5 ml. of concentrated hydrochloric acid. Stopper the flask, mix, and exactly 30 seconds after the acid addition add 10 ml. of 15 per cent potassium iodide. Titrate with standard thiosulfate.

Notes: (1) The bromate-bromide solution contains 5.568 g. of potassium bromate and 30 g. of potassium bromide per liter.

(2) Ellington and Beard[187] substituted carbon tetrachloride for ethanol. They

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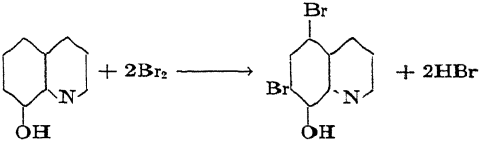
[186] H. Levenson, *Ind. Eng. Chem., Anal. Ed.*, 2, 246 (1930).

[187] O. C. Ellington and H. G. Beard, *J. Soc. Chem. Ind. (London)*, **50**, 151T, (1931).

state that the conditions are not then so critical because this solvent is less reactive. Diphenylamine can be determined in this way; 4 atoms of bromine are substituted if a 50 per cent excess of bromine is present. Under the same conditions, *p*-toluidine and aniline substitute 2 atoms of bromine.

(3) Glacial acetic acid is said to be better than either of the two preceding solvents.[188] It is unreactive to bromine and allows the reaction to proceed in a single phase.

5. Determination of Hydroxyquinoline and Its Application to the Determination of Metals. *8-Hydroxyquinoline* (*Oxine*): According to Berg,[189] hydroxyquinoline forms a dibromosubstitution product with bromine.



Procedure: Mix the solution containing 8–10 per cent of hydrochloric acid with some drops of .1 per cent indigo carmine solution and titrate with bromate-bromide solution until the color changes from blue through green to yellow. Then add bromate solution in excess, dissolve potassium iodide in the solution, and finally titrate with thiosulfate, using starch as indicator. One milliliter of $0.1N$ bromate corresponds to 3.63 mg. of *o*-hydroxyquinoline.

After the addition of the iodide, a chocolate brown precipitate of the iodine addition product is formed which decomposes on titration with thiosulfate. If much oxine was originally present, crystals of the dibromo substitution product separate out. Kolthoff found that the method gives excellent results if the back-titration is carried out in less than 10 minutes. He preferred to use methyl red as indicator. Again, a direct titration is not feasible, for the color change from red to yellow is not at all sharp; however, the addition of excess of bromine is easily observed. It is advisable to titrate the solution containing 0.5 g. of potassium bromide and 1–2 drops of 0.2 per cent methyl red slowly until the solution is pure yellow.

Fleck, Greenane, and Ward[190] obtained irregular results if the dibromohydroxyquinoline separated out; probably some iodine was adsorbed. For titration, they added 20 ml. of concentrated hydrochloric acid to 80 ml. of solution followed by a slight excess of bromate with shaking. After 5 minutes, 15 ml. of carbon disulfide was added (chloroform or carbon tetrachloride cannot be used). After the addition of 10 ml. of 10 per cent potassium iodide the solution was titrated with 0.1N thiosulfate, starch being used as indicator. A sharp color change to yellowish green was observed in the aqueous layer. When the concentration of oxine was so small that no precipitation occurred after the addition of iodide, the carbon disulfide was not used.

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[188] T. D. Waugh, G. Harbottle, and R. M. Noyes, *Ind. Eng. Chem.*, *Anal. Ed.*, **18**, 636 (1946); cf. I. S. Hirschhorn, *Anal. Chem.*, **19**, 880 (1947).

[189] R. Berg, *Pharm. Ztg.*, **71**, 1542 (1926).

[190] H. R. Fleck, F. J. Greenane, and A. M. Ward, *Analyst*, **59**, 325 (1934).

Kampf[191] claimed that the end-point could be detected directly with methyl red as indicator if the hydrochloric acid concentration was above 15 per cent. Near the end-point, the color changed from red to orange. At this point, Kampf added 2 more drops of indicator, allowing 15 seconds before continuing the titration. He then continued to add 2 drops of indicator and to titrate until the color changed to an orange and then to yellow 15 seconds after the addition of the indicator. The amount of bromate used up by the indicator was deducted. Schulek and Clauder[192] recommended the following method.

Procedure: Dissolve the sample containing 20–40 mg. of *o*-hydroxyquinoline in a little hydrochloric acid in a 500 ml. bromine flask (Fig. 5, p. 29) and make the solution slightly alkaline with sodium hydroxide. A strip of litmus paper acts as indicator. Dilute with water to 50 ml., dissolve 0.5 g. of potassium bromide in the mixture, and add 0.1N potassium bromate from a burette to give an excess of 10–20 per cent. Close the flask and add water containing 0.5 g. of potassium iodide to the cup to cover the stopcock. Open the cock and suck some air out with the mouth to form a partial vacuum in the flask. Place 10 ml. of concentrated hydrochloric acid in the small receiver and carefully run this into the flask. Rinse the receiver several times with a little water and fill it with 5 ml. of water containing 2.5 g. of potassium iodide. Set the flask in the dark for 5 minutes, cool (if necessary), then run in the iodide solution, shake thoroughly, dilute with 300 ml. of water, and titrate with 0.1N thiosulfate.

Notes: (1) The authors give methods for the isolation of *o*-hydroxyquinoline from medicinal preparations by distillation or by extraction.

(2) Smith[193] prepared the 0.1N bromate in water containing 1.2 per cent of potassium bromide and 0.0125 per cent of indigo carmine. Although part of the color of the indicator fades during the titration, new indicator is added continuously with the bromate. As the indigo uses up some bromine, the bromate solution must be standardized. Smith also states that the addition of carbon disulfide is not necessary if the acidity at the end-point is 2–3N.

Poethke[194] preferred arsenite for the back-titration with either *p*-ethoxychrysoidine or brilliant carmoisine as indicator.

Procedure: Dissolve the oxine (or metal oxinate) in 12.5 per cent hydrochloric acid and add sufficient water to make the acidity less than 5 per cent in this acid. Add 0.5–1 g. of potassium bromide, 1–2 drops of methyl red and sufficient bromate solution just to bleach the indicator. Add 1–2 ml. in excess. Add a suitable excess of standard arsenite, 1–4 drops of a 0.1 per cent solution of one of the above indicators and continue the titration to the color change.

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[191] L. Kampf, *Ind. Eng. Chem., Anal. Ed.*, 13, 72 (1941).

[192] E. Schulek and O. Clauder, *Z. anal. Chem.*, **108**, 385 (1937).

[193] G. S. Smith, *Analyst*, 64, 577 (1939).

[194] W. Poethke, *Pharm. Zentralhalle*, 86, 2 (1947).

Notes: (1) Satisfactory results were obtained even with 0.01*N* bromate solution.

(2) Belcher[195] used a similar method but preferred α-naphthoflavone as indicator. However, he found that the amount of oxine which could be determined in this way was limited to about 25 ml. of 0.1*N* oxine. Above this amount the yellow color of the oxine masked the color change of the indicator.

Determination of Metals as Oxines: Studies by Hahn and by Berg[196] have shown that 8-hydroxyquinoline (named oxine by Hahn) yields very difficultly soluble crystalline compounds of the type $(C_9H_6ON)_2M$ (M = divalent metal) with various metals. These reactions are very sensitive; they have found great application in quantitative analysis. For a comprehensive account of the uses of oxine, the treatise by Hollingshead[197] should be consulted.

The oxine compounds are filtered on a Jena glass filter of porosity G3 to 5; the filtration and washing are extremely rapid and a complete determination can be done in 15 minutes. The flask and the precipitate are washed until the filtrate is colorless; the filter is then transferred to the original vessel, the precipitate is dissolved in 10–15 ml. of boiling 4*N* hydrochloric acid, and the funnel and filter are washed with water. The filter can then serve for another determination. The solution in the flask is cooled, methyl red and 0.5 g. of potassium bromide are added, and the solution is titrated with bromate (p. 549).

For the precipitation of 1 millimole of a divalent metal, about 7 ml., and, of a trivalent metal, about 10 ml. of 5 per cent alcoholic solution of oxine suffice. This solution should be prepared freshly every week and stored in a brown glass bottle. One millimole of a divalent metal corresponds to 80 ml., and, of a trivalent metal 120 ml., of 0.1*N* bromate solution. In general, the solution should not contain more than 100–200 mg. of metal in 100 ml. for the precipitation.

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[195] R. Belcher, *Anal. Chim. Acta*, 3, 578 (1949).

[196] R. Berg, *Z. anal. Chem.*, 70, 341 (1926); *J. prakt. Chem.*, 115, 178 (1927); F. L. Hahn, *Chem. Ztg.*, 50, 754 (1926), *Z. angew. Chem.*, 39, 1198 (1926); cf. J. E. Saul and D. Crawford, *Analyst*, 43, 348 (1918); N. Schoorl, *Pharm. Weekblad*, 56, 325 (1919); C. T. Mörner, *Pharm. Zentralhalle*, 63, 399 (1922); I. M. Kolthoff, *Chem. Weekblad*, 24, 606 (1927); F. L. Hahn and K. Vieweg, *Z. anal. Chem.*, 71, 122 (1927); R. Berg, "*Das o-Oxychinolin (Oxin)*," in Vol. XXXIV of *Die Chemische Analyse*, W. Bottger, ed., Enke, Stuttgart, 1935.

[197] R. G. W. Hollingshead, *Oxine and Its Derivatives*, Butterworths, London, Vols. I and II, 1954, Vols. III and IV, 1956.

Fleck and Ward[198] determined the pH range in which a quantitative precipitation of various metals is found. Gotô[199] has made a similar study; the results of both groups of investigators are given in Table VI. For the precipitation of metal oxinates in varying concentrations of sodium hydroxide and tartrate the paper by Gotô and Kakita[200] should be consulted. Fleck[198] gives the following procedure to obtain the correct pH in various precipitations.

TABLE VI

Precipitation pH of Metallic Oxinates

	Values of Fleck and Ward		Values of Gotô	
Metal	pH a[a]	pH b[b]	pH a	pH b
Aluminum	—	—	2.84–3.15	4.39–9.8
Bismuth	—	—	3.5 –3.8	4.8 –9.4
Cadmium	4.5	5.66–14.58	4.0 –4.29	5.41–13.26
Calcium	—	—	6.11–7.4	9.21–12.69
Cobalt	4.10	4.33–14.5	3.12	4.2 –11.6
Copper	3.45	5.33–14.55	2.2 –2.5	3.3→
Iron(III)	—	—	2.4 –2.6	2.8 –11.2
Lead	—	—	4.81–5.1	8.44–12.28
Magnesium	7.26–7.71	9.44–12.66	6.7 –7.4	8.16→
Manganese	—	—	4.25–4.55	5.87–9.51
Molybdenum	3.08–3.28	3.6 –7.33	0.7 –1.0	3.3 –7.6
Nickel	4.10–4.33	4.48–14.58	2.77–3.10	4.57–9.97
Thorium	3	—	3.74–4.07	4.43–8.80
Titanium	—	—	3.50–3.72	4.79–8.59
Tungsten	3.46–3.52	4.95–5.65	—	—
Uranium	4.45–4.52	5.71–9.81	3.07–3.43	4.07–8.84
Vanadium	—	—	1.2	2.7 –6.1
Zinc	3.94–4.2	4.58–13.4	2.84–3.10	4.39→

[a] pH a = pH of initial precipitation.
[b] pH b = pH range of complete precipitation.

Procedure: Dilute the neutral solution of the metal to 110 ml. and add 25 ml. of 20 per cent ammonium acetate and 10 ml. of 2 per cent oxine solution in *N* acetic acid. Heat the solution to boiling and then add with stirring in a fine stream the necessary amount of boiling hot acid or alkali (to obtain the suitable pH) from a beaker.

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[198] H. R. Fleck and A. M. Ward, *Analyst*, **58**, 388 (1933); H. R. Fleck, *ibid.*, **62**, 378 (1937).

[199] H. Gotô, *J. Chem. Soc. Japan*, **54**, 725 (1933); **56**, 314 (1935); *Science Repts. Tôkoku Imp. Univ., First Ser.*, **26**, 391, 418 (1937).

[200] H. Gotô and Y. Kakita, *J. Chem. Soc. Japan*, **62**, 915 (1941).

Amount of Acid or Alkali Required for Standardization of pH:

ml. glacial acetic acid	0	1	2	3	4	5	10	20
pH given	4.9	4.8	4.7	4.6	4.5	4.4	4.1	3.6

ml. 1*N* NaOH	0	5	10	15	20	30	40	50	60	80	100
pH given	4.9	5.6	6.3	7.4	8.3	8.9	9.4	9.8	11.6	12.3	13.2

After the addition of the acid or sodium hydroxide, boil for 5 minutes and then filter the precipitate in a glass filter funnel (G3). Wash the precipitate with 250 ml. of boiling water, dissolve it in 50 ml. of 6*N* hydrochloric acid, and titrate the solution after diluting with 50 ml. of water.

It should be noted that the acidity levels at which metals no longer precipitate are only valid for pure solutions. In a mixture of two metals, one can be partially coprecipitated with the other, although it should not, and when alone will not, precipitate at the pH used. Thus magnesium oxine will precipitate when the pH is equal to or greater than 7.5. However, Moyer and Remington[201] found that some magnesium precipitates with zinc if zinc is precipitated at pH greater than 5.5, but that at lower pH (4.6–5.5) satisfactory results could be achieved. They also found that ferric iron could be quantitatively precipitated in presence of aluminum at a pH between 3.5 and 4. Frequently the coprecipitation can be ascribed to adsorption.

It can be seen that there are some discrepancies between the results obtained by Gotô and by Fleck and Ward; this may be accounted for by the somewhat different conditions under which the results were obtained. More recently these pH ranges have been reinvestigated, particularly by Borrel and Pâris.[202] Their results are given in Table VII and those of various other investigators in Table VIII.

TABLE VII

pH Range for Complete Precipitation of Metal Oxinates According to Borrel and Pâris

Metal	pH
Aluminum	4.7→
Cadmium	5.5→
Cobalt	4.9→
Magnesium	8.7→
Nickel	4.6→
Vanadium	4.5
Zinc	4.5

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[201] H. V. Moyer and W. J. Remington, *Ind. Eng. Chem., Anal Ed.*, **10**, 212 (1938).

[202] M. Borrel and R. A. Pâris, *Anal. Chim. Acta*, **4**, 279 (1950); **6**, 387, 393, 394 (1952).

Although it is possible to determine many metals by oxine procedures it is doubtful if more than a few metals are ever determined in this way, for better alternative procedures are usually available.

TABLE VIII

pH Range for Complete Precipitation of Metal Oxinates

Metal	pH	Reference
Bismuth	5.2→	H. G. Haynes, *Analyst*, **70**, 129 (1945).
	6.5	J. Gillis, J. Eeckhout, and G. Standaert, *Mededeel. Vlaam. Acad. Kl. Wetenschap.*, No. 7, 3 (1940).
Calcium	9.2→	R. Näsänen, *Acta Chem. Scand.*, **5**, 1293 (1951).
	9.5–10	J. Reinasiewicz and M. E. Polley, *Anal. Chem.*, **21**, 1398 (1949).
Gallium	3.1→[a]	T. Moeller and A. J. Cohen, *ibid.*, **22**, 686 (1950).
Indium	2.5–3.0	W. Geilmann and Fr. W. Wrigge, *Z. anorg. Chem.*, **209**, 129 (1932).
Iron(III)	4.1	R. C. Chirnside, C. F. Pritchard, H. P. Rooksby, *Analyst*, **66**, 399 (1941).
Plutonium(VI)	*ca.* 5	G. B. Harvey, H. G. Heal, A. G. Maddock, and E. L. Rowley, *J. Chem. Soc.*, **1947**, 1010.
Scandium	6.5–8.5[b]	L. Pokras and P. M. Bernays, *J. Am. Chem. Soc.*, **73**, 7 (1951).
Thallium(III)	4–8	T. Moeller and A. J. Cohen, *Anal. Chem.*, **22**, 686 (1950).
Tungsten	3.3–3.5	S. Halberstadt, *Compt. rend.*, **205**, 987 (1937).
	5	R. Přibil and V. Sedlar, *Collection Czech. Chem. Communs.*, **16**, 69 (1951).
Uranium	5–9	A. Claassen and J. Visser, *Rec. trav. chim.*, **65**, 211 (1946).

[a] pH 7–7.5 recommended.
[b] pH 7.5 recommended.

Accordingly, only a selection of the commoner determinations will be given here. For details of other oxine procedures the treatise by Hollingshead[197] should be consulted.

Aluminum. Berg[203] found that aluminum could be precipitated from acetic acid solutions or ammoniacal solutions containing tartrate. Several variations of his procedure have been described. Knowles[204] recommends the following method.

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[203] R. Berg, *Z. anal. Chem.*, **71**, 369 (1927); cf. F. L. Hahn and K. Vieweg, *ibid.*, 122.

Procedure: To the aluminum solution containing not more than 0.1 g. of aluminum in 200 ml., add 10 ml. of hydrochloric acid and tartaric acid equal to five times the amount of aluminum present. Add 6 g. of ammonium acetate dissolved in 15 ml. of water and 8–10 drops of 0.04 per cent ethanolic bromocresol purple. Add 1:1 ammonia solution until the indicator turns purple. Stir and slowly add oxine solution (dissolve 12.5 g. in 25 ml. of hot glacial acetic acid and pour into 450 ml. of water at 60°C.; cool, filter if necessary, and dilute to 500 ml.) to give a 15–25 per cent excess. Heat to boiling while stirring occasionally and boil gently for 1 minute. Cool to 60°C., filter with moderate suction on a G4 sintered-glass crucible, and wash with 100 ml. of cool water. Place the crucible in a 600 ml. beaker, add 200 ml. of 1:4 hydrochloric acid, heat to dissolve the precipitate, and rinse and remove the crucible. Recover the solution from the frit by sucking through warm 1:9 hydrochloric acid. Dilute to 400 ml., cool to room temperature, and titrate with $0.1N$ or N bromate-bromide solution (containing 100 g. of potassium bromide per liter) to give an excess of 2–3 ml. Stir, allow to stand for 30–60 seconds, add 15 ml. of 20 per cent potassium iodide solution, and titrate with $0.1N$ thiosulfate, adding starch in the usual way. One milliliter of $1N$ bromate corresponds to 2.2475 mg. of aluminum.

Notes: (1) For up to 10 mg. of aluminum use $0.1N$ bromate and $1N$ bromate for 50–100 mg.

(2) For the determination of aluminum in presence of beryllium, Knowles[204] omits the addition of tartaric acid. The procedure can be applied to the analysis of feldspars.

(3) Balanescu and Motzoc[205] recommended precipitation from slightly alkaline solution, especially in the presence of phosphoric acid and when small amounts of aluminum are present. Add N sodium hydroxide dropwise until the precipitate just dissolves (or with small amounts until phenolphthalein turns pink) and dilute to 90–100 ml. Warm to 40–50°C. and add an excess of alcoholic 5 per cent oxine solution. Heat to boiling and filter hot after standing for a short time.

(4) In order to prevent precipitation of part of the aluminum (and also of ferric iron) as basic acetate, Kampf[206] recommends the addition of a small amount of tartrate. He adds 5 ml. of 20 per cent tartaric acid, neutralizes to methyl red, adds 20 ml. of 25 per cent ammonium acetate solution, brings to the boil, and precipitates. Care should be observed with the procedure, for the solubility of aluminum oxinate is increased by tartrate.

Magnesium: Magnesium oxinate is not precipitated from acid solution but precipitates quantitatively from ammoniacal solution.[207] The results, however, tend to be high because of coprecipitation of oxine, but vary with the manner of precipitation. Miller and McLennan[208] found the best results by the following method.

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[204] H. B. Knowles, *J. Research Natl. Bur. Standards*, **15**, 87 (1935); cf. R. C. Chirnside, C. F. Pritchard, and H. P. Rooksby, *Analyst*, **66**, 399 (1941).

[205] G. Balanescu and M. D. Motzoc, *Z. anal. Chem.*, **91**, 188 (1932).

[206] L. Kampf, *Ind. Eng. Chem., Anal. Ed.*, **13**, 72 (1941).

[207] Cf. R. Berg, *Z. anal. Chem.*, **71**, 23 (1927); F. L. Hahn and K. Vieweg, *ibid.*, 122, I. M. Kolthoff, *Chem. Weekblad*, **24**, 606 (1927); J. ten Have, *Chem. Weekblad*, **44**, 721 (1948).

Procedure: To 100 ml. of solution containing 10–50 mg. of magnesium oxide add 2 g. of ammonium chloride, a few drops of ethanolic 0.02 per cent *o*-cresolphthalein indicator and 6*N* ammonia to give an excess of at least 2 ml. over that needed to give a violet color (pH 9.5). Heat to 70–80° C. and add a 5 per cent (or 1 per cent for small amounts of magnesium) oxine solution in 2*N* (or 0.4*N*) acetic acid *very slowly* with constant stirring until precipitation is complete and a *small* excess is present which is indicated by the yellow color of the supernate. Digest for 10 minutes on a steam bath, filter the hot solution, and wash with hot water. Dissolve the precipitate in 2*N* hydrochloric acid and titrate. (With large amounts of magnesium, dilute the solution and use an aliquot.)

Notes: (1) With 5–13 mg. of magnesium Miller and McLennan obtained excellent results, but with 2.5 mg. the results were about 2 per cent high. The positive error increased with decreasing amount of magnesium.

(2) Fleck and Ward[198] precipitated the magnesium quantitatively from ammonium acetate-ammonia solution at pH values of 9.5 to 12.6.

(3) Calcium interferes; Berg[207] recommended a further precipitation after dissolving the precipitate. Hahn and Hartleb[209] separated the calcium with oxalic acid, neutralized and, without prior filtration, precipitated the magnesium as the oxine. It is best to add a slight excess of oxalic acid dropwise to the hot solution and neutralize the excess with much ammonia. Kolthoff[207] obtained very satisfactory results in this way. The effect of large amounts of oxalate was studied by Miller and McLennan[208] in connection with the determination of magnesium in rocks.

(4) Arnoux[210] has described the separation of magnesium and ferric iron by extracting the oxines with chloroform; the iron oxine dissolves. The solubility of various oxines in 96 per cent ethanol has been studied.[211]

(5) Fischinger[212] claimed good results by titrating directly with bromate: he found, however, that internal indicators were unsatisfactory and used starch-iodide paper as an external indicator.

Several minor variations of the iodometric back-titration procedure have been described.[213]

(6) The bromometric titration of magnesium oxinate has been applied to a host of determinations, particularly in the field of metallurgical analysis. It is not within the province of this book to describe these methods, and the appropriate textbooks or the treatise of Hollingshead[197] should be consulted for details.

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[208] C. C. Miller and I. C. McLennan, *J. Chem. Soc.*, **1940**, 656.

[209] F. L. Hahn and E. Hartleb, *Z. anal. Chem.*, **71**, 226, (1927).

[210] M. Arnoux, *Compt. rend. soc. biol.*, 116, 436 (1934).

[211] M. Javillier and J. Lavollay, *Ann. fals. et fraudes*, **27**, 326 (1934).

[212] Fischinger, *Gesundh. Ing.*, **70**, 85 (1949).

[213] F. L. Hahn, *Z. anal. Chem.*, 86, 153 (1931); D. M. Greenberg, C. Anderson, and E. V. Tufts, *J. Biol. Chem.*, **111**, 561 (1935); T. Honjo, *Nippon Kinzoku Gakkai-Shi*, **B15**, 444 (1951); *Chem. Abstr.*, **47**, 12112 (1953); G. Cruess-Callaghan, *Biochem. J.*, 29, 1081 (1935) (micro scale); T. Akiyama, and M. Fujiwara, *J. Pharm. Soc. Japan*, **73**, 785 (1953); *Chem. Abstr.*, **47**, 12112 (1953).

Zinc:[214] To the solution add 5 ml. of $4N$ acetic acid, 5 ml. of $2N$ sodium acetate, and an excess (recognized by the yellow color of the solution) of oxine solution. Heat to boiling, set aside for 2 minutes (Kolthoff finds that longer standing is unnecessary), and filter. Proceed as given previously.

Notes: (1) Even 20 mg. of zinc per liter can be determined accurately, e.g., zinc in drinking water. Large amounts of calcium, magnesium, alkali metals do not interfere.

(2) According to Fleck and Ward,[198] zinc is quantitatively precipitated by oxine from ammonium acetate solution with excess of acetic acid or ammonia at pH 4.6–13.6. In the latter case an excess of sodium hydroxide is present and the zinc is present as zincate.

(3) If the solution contains ferric or chromic ions or aluminum, Berg[214] found that the precipitation is satisfactory from solutions containing $0.2N$ sodium hydroxide and 3–5 per cent of tartrate. If large amounts of cobalt, nickel, manganese, lead, and bismuth are present, a further precipitation from alkaline solution is necessary. Mercury can be complexed with potassium cyanide. The separation of zinc from copper and cadmium is not readily achieved by the described method.

(4) Wiggins and Wood[215] described a method for the determination of zinc in the presence of uranium.

Cadmium: Precipitation by the method of Fleck (p. 552) gives a precipitate of composition $Cd(C_9H_6ON)_2 \cdot xH_2O$; the yield is quantitative in the pH range 5.7–14.6. Berg[216] recommends the following method.

Procedure: To the neutral or slightly acid solution add sodium carbonate solution until a turbidity is obtained. Remove this by adding acetic acid. Add 3–5 g. of sodium acetate dissolved in a small amount of water and precipitate cadmium oxinate by the addition of a slight excess of a 2 per cent ethanolic or 4 per cent acetone solution of oxine. Heat just to boiling and allow to settle. Filter off the precipitate, wash first with warm, then with cold, water. Dissolve the precipitate and titrate in the usual way.

Uranium: Uranyl in neutral or slightly acid solution (ammonium acetate-acetic acid buffer) gives a deep red precipitate with oxine which is said to have the composition $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$.[217] The precipitation is carried out at boiling point, and the mixture is cooled, filtered, and washed first with hot water to remove the excess of oxine and then several times with cold water. Claassen and Visser[218] reported low results by this procedure which they ascribed to the solubility of the precipitate in the wash water. They recommended instead that the precipitate be washed with an aqueous solution of oxine.

Procedure: Neutralize the uranium solution with dilute ammonia solution to give a slight turbidity. (If tartrate is present, the solution remains clear; adjust to a pH of about 6 using an indicator.) Add 20–25 ml. of 20 per cent ammonium acetate, dilute to 100–200 ml., and heat to boiling. Add dropwise a 4 per cent solution of oxine in 1.5*N* acetic acid with constant stirring to give an excess of 4–5 ml. (use 0.5 ml. per 10 mg. of uranium). Stir until crystalline. Add dropwise while stirring the same volume of *N* ammonium hydroxide solution to neutralize most of the acetic acid and boil for 1–2 minutes. Allow to cool to 40°C. If less than 10 mg. of uranium is present, digest until the supernatant liquid is clear and then cool to 40°C. Filter on a sintered-glass crucible (G4) and wash with 50–150 ml. of hot 0.04 per cent aqueous oxine solution. Dissolve the precipitate in 2*N* hydrochloric acid and titrate in the usual way.

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[214] R. Berg, *Z. anal. Chem.*, **71**, 171 (1927).

[215] W. R. Wiggins and C. E. Wood, *J. Soc. Chem. Ind.*, **53**, 254 T (1934).

[216] R. Berg, *Z. anal. Chem.*, **71**, 321 (1927).

[217] F. Hecht and W. Reich-Rohrwig, *Monatsh.*, **53/54**, 596 (1929); cf. F. J. Frere, *J. Am. Chem. Soc.*, **55**, 4362 (1933).

[218] A. Claassen and J. Visser, *Rec. trav. chim.*, **65**, 211 (1946).

Notes: (1) The procedure is accurate to 0.2 per cent for more than 50 mg. of uranium; for less, it is accurate to 0.1 mg. It allows a satisfactory separation from magnesium, alkali, and alkaline earth metals.

(2) In the Manhattan Project literature,[219] methods are described for precipitation from acetate buffered solution (pH 5–6) or from ammoniacal solution. The precipitate is washed with 2 per cent ammonium nitrate solution.

(3) Fleck[220] found that the precipitation is quantitative over the pH range 5.7 to 9.8. He also described a separation of uranium and molybdenum.

Procedure: Boil 80 ml. of the solution containing 5 g. of ammonium acetate and add 7 ml. of glacial acetic acid and 10 ml. of 2 per cent oxine solution. Boil for 5 minutes, and filter off the molybdenum complex. To the boiling filtrate add 10 ml. of 2 per cent oxine solution and 30 ml. of 5*N* sodium hydroxide, which quantitatively precipitates the uranium.

Thorium: An orange-red compound is formed by the interaction of a thorium salt with oxine.[217] There has been some controversy about the composition of this precipitate.[197,217,221] Like the uranyl salt, an addition compound is formed, Th $(C_9H_6NO)_4 \cdot C_9H_7NO$. Hecht and Ehrmann[221] state that precipitation is best from acetic acid-acetate medium; the usual bromometric titration can be applied after the precipitate has been dissolved in hydrochloric acid.[222]

Tungstate, Molybdate, and Vanadate: A number of investigations on the quantitative precipitation of these ions is described by Nieriker and Treadwell.[223] Under the conditions of the method, tungsten is precipitated as $WO_2(C_9H_6ON)_2$, molybdenum as $MoO_2(C_9H_6ON)_2$, and vanadium as $V_2O_3(C_9H_6ON)_4$.

Procedure: Heat the solution, which should be 0.01*M* in phosphoric acid, to boiling and add a 50–100 per cent excess of 4 per cent oxine solution in 50 per cent alcohol, followed by saturated sodium acetate solution until a pH of 5.3 is attained. Boil the mixture for a few minutes and, when the precipitate has settled, filter on a sintered-glass crucible and wash with hot water. Dissolve the vanadium oxine in dilute phosphoric or hydrochloric acid (the ferric compound is also soluble) and the molybdenum and tungsten compounds in warm concentrated phosphoric acid. Titrate the oxine in the solution in the usual way.

Tungsten in Presence of Iron: Precipitate the iron(III) with oxine from a weakly alkaline solution containing 0.5–2 ml. of glycerol. Add enough oxine to the filtrate to precipitate the tungsten, heat the mixture to boiling, and add 2*N* acetic acid to give a pH of about 5.5. Too much glycerol keeps some of the iron in the alkaline solution; this iron precipitates with the oxine in acid medium.

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[219] *Analytical Chemistry of the Manhattan Project*, C. J. Rodden, ed., McGraw-Hill, New York, 1950, pp. 51, 75.

[220] H. R. Fleck, *Analyst*, 62, 378 (1937).

[221] Cf. F. Hecht and W. Ehrmann, *Z. anal. Chem.*, 100, 98 (1935).

[222] Cf. ref. 219, p. 187.

[223] R. Nieriker and W. D. Treadwell, *Helv. Chim. Acta*, 29, 1472 (1946).

Notes: (1) The molybdate and tungstate compounds are not readily soluble in the usual acids. Montequi and Doadrio[224] dissolved the oxine molybdate in 2*N* sodium hydroxide solution before applying the usual bromometric titration. Přibil and Sedlář[225] state that the tungstate dissolves in 4*N* sodium hydroxide; it is necessary also to add oxalic acid to prevent precipitation of tungsten during the titration.

Procedure: Dissolve the precipitate in hot 4*N* sodium hydroxide solution. Add 10–20 ml. of a 15 per cent solution of oxalic acid and neutralize to methyl red with 4*N* hydrochloric acid. Add 15 ml. in excess. Titrate with 0.1*N* bromate solution until the indicator is bleached, add 4 ml. in excess, and back-titrate iodometrically.

(2) Přibil and Malat[226] have shown that in the presence of ethylenediaminetetraacetic acid the precipitation of tungstate and molybdate is not affected by many of the usual interfering metals, e.g., aluminum, iron, and chromium(III).

Silicon: Merz[227] determined silicon by precipitating as oxine silicomolybdate and titrating the excess oxine bromometrically. An empirical standardization was necessary. McHard *et al.*[228] applied the procedure to the determination of silicon in organic compounds.

The original papers should be consulted for details.

Titanium:[229] Titanium(IV) is quantitatively precipitated by oxine from a solution containing alkali acetate, acetic acid, and tartrate or from an ammoniacal tartrate solution. The precipitate has the composition $TiO(C_9H_6NO)_2$.

Procedure: Dilute the solution to 150 ml. after adding 0.5–1 g. of tartaric acid (an excess over that needed for complex formation) and 0.5 g. of sodium acetate, and neutralize to phenolphthalein with ammonia; acidify with 1–2 ml. of acetic acid per 100 ml. of solution. Heat to 60°C. and precipitate the titanium with excess of alcoholic 3 per cent oxine solution. Boil the solution for about 10 minutes (this is necessary to obtain the precipitate in large crystals). Collect the hot precipitate on a G3 sintered-glass crucible and wash with hot water until the filtrate is colorless. Dissolve the precipitate in concentrated hydrochloric acid, add water to give a 2*N* acid solution, and titrate with bromate.

Notes: (1) Even very small amounts of titanium (0.5–1 mg.) can be accurately determined in this way.

(2) The procedure is applicable in the presence of the alkaline earths and magnesium.

(3) *Separation of Aluminum:* In presence of malonic acid, aluminum remains in solution and titanium is quantitatively precipitated. To the test solution, add 1 g. of tartaric acid and 70–80 times the amount of malonic acid which is necessary to complex the aluminum. Add 1 g. of sodium acetate, dilute to 150 ml., neutralize with ammonia, and continue the above procedure. Determine the aluminum in the filtrate by dropwise addition of a 3 per cent oxine–acetate solution and ammonia at about 50°C. until there is a distinct smell of ammonia. Heat for a

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[224] R. Montequi and A. Doadrio, *Anales fis. y quim. (Madrid)*, **43**, 1141 (1947).

[225] R. Přibil and V. Sedlář, *Collection Czech, Chem. Communs.*, **16**, 69 (1951).

[226] R. Přibil and M. Malat, *Collection Czech Chem. Communs.*, 15, 120 (1950).

[227] J. A. Merz, *Svensk Kem. Tidskr.*, **53**, 374 (1941).

[228] J. A. McHard, P. C. Servais, and H. A. Clark, *Anal. Chem.*, **20**, 325 (1948).

[229] R. Berg and M. Teitelbaum, *Z. anal. Chem.*, **81**, 1 (1930).

short time at 80°C. Filter the precipitate, wash, etc. (p. 555). The dissolution of the precipitate is very slow in concentrated hydrochloric acid but is almost immediate in alcoholic hydrochloric acid solution (1 part of alcohol to 1 part of concentrated acid). Titrate the liberated iodine immediately after the addition of bromate to avoid any reaction of bromine with alcohol.

(4) Claassen and Visser[230] stated that precipitation of titanium was incomplete and the precipitate passed through the filter when washed. They claimed that if the pH was adjusted to 6.3–6.5 (bromocresol purple indicator) and ammonium sulfate solution was used for washing the precipitate, satisfactory results were obtained. Stuckert and Meier,[231] however, reported that the Berg-Teitelbaum procedure given above was satisfactory provided that silica was removed first.

Iron (Ferric): According to Berg,[232] iron in presence of alkali acetate in 25 per cent acetic acid is quantitatively precipitated at boiling temperatures as $Fe(C_9H_6ON)_2 \cdot xH_2O$; it also precipitates from 15–20 per cent acetic acid in the cold or on moderate heating (see below). The precipitate is dissolved in hydrochloric acid and 10 ml. of 50 per cent phosphoric acid is added to prevent the interference of iron in the back-titration of the bromine. Poethke[194] preferred the arsenite method for the back-titration (p. 550).

Iron in Presence of Aluminum: Hydroxycarboxylic acids form complexes with iron and aluminum. According to Berg, it is possible to find conditions by which iron is quantitatively precipitated and aluminum is found only in the filtrate.

Small Amounts of Aluminum and Large Amounts of Iron: To about 100 ml. of solution, add 3 g. of ammonium acetate and 3–4 g. of ammonium tartrate. Add acetic acid so that its concentration after the precipitation will be 15–20 per cent. Precipitate at about 50°C. by dropwise addition of a known excess of oxine solution. Cool, dilute to 150 ml., filter, and determine the unconsumed oxine in the filtrate. In another aliquot, precipitate the aluminum from slightly ammoniacal solution.

Large Amounts of Aluminum in Presence of Iron: Carry out the separation from acetic acid solution containing malonic acid. Iron is precipitated in presence of 0.5–1.5 g. of sodium malonate in 5–10 per cent acetic acid. The back-titration method is impossible here, for malonic acid is also brominated

Moyer and Remington[201] and Chirnside *et al.*[204] state that coprecipitation of iron and aluminum oxinates occurs under all conditions. The latter workers concluded that separation of iron and aluminum with oxine was possible only in a very narrow pH range under controlled conditions.

The determination of iron in presence of alkaline earths causes no difficulty so long as the acetic acid concentration is 5–10 per cent; in the presence of manganese it should be 10 per cent.

Calcium: In the presence of much ammonium salt, calcium can be quantitatively precipitated as the oxine from ammoniacal solution.[233] The solution is heated to boiling, 1–2 ml. of 6*N* ammonia is added with an excess of oxine, and the precipitate is filtered after 5 minutes. For solutions which are less than 0.005*M* in calcium, some hours should elapse before filtration. Barium does not interfere, but coprecipitation occurs with strontium so that in presence of this metal reprecipitation is necessary.

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[230] A. Claassen and J. Visser, *Rec. trav. chim.*, 60, 715 (1941).

[231] L. Stuckert and F. W. Meier, *Sprechsaal*, 68, 527 (1935).

[232] R. Berg, *Z. anal. Chem.*, 76, 191 (1929).

[233] I. M. Kolthoff, *Chem. Weekblad*, 24, 606 (1927).

Manganese.[232]

Procedure 1: To the manganese solution, add enough alkali acetate (1-2 g. sodium acetate per 50 mg. of Mn) and, after adding some drops of sulfur dioxide solution or 0.1–0.2 g. of hydroxylamine hydrochloride, make the solution slightly alkaline to phenolphthalein. Bleach the solution with acetic acid, heat to 60–70°C., and add an excess of alcoholic oxine solution. Heat to boiling and filter after heating for 15 minutes on a steam bath.

Procedure 2. Warm the manganese solution containing mineral or acetic acid and add excess of oxine acetate solution. Gradually raise the temperature and drop in dilute ammonia with constant stirring until there is a permanent smell of ammonia. Proceed further as in the first method. The method tends to give slightly high results.

Notes: (1) Manganese in the presence of calcium, barium, and strontium is determined by the first method; separation of magnesium is unnecessary.

(2) Manganese in presence of zinc is determined by precipitating zinc in hot 6 per cent acetic acid solution and determining manganese in the filtrate. When nickel is present it is precipitated from hot 8–10 per cent acetic acid solution.

Nickel and Cobalt: These are precipitated from neutral or slightly acetic acid solutions.[234] If the precipitation is done from acid ammonium acetate solution, and if, after the addition of oxine, sodium hydroxide is added, cobalt and nickel are quantitatively precipitated between pH 4.5 and 14.5. Copper is precipitated between pH 5.3 and 14.5. According to Fleck and Ward,[198] nickel and magnesium can be determined singly, if the nickel is first precipitated from ammonium acetate–acetic acid solution, and the magnesium is determined in the filtrate after the addition of sodium hydroxide.

Cerium (III): In ammoniacal solution containing tartrate, cerous salts give a yellow crystalline precipitate of the formula $Ce(C_9H_6ON)_3$.[235]

Procedure: Add 1 g. of hydroxylamine hydrochloride to the solution which contains 10–50 mg. of cerium(IV) and heat until the solution is colorless. Add 10 ml. of a concentrated sodium tartrate solution, 20 ml. of 2*N* ammonia and dilute to 100 ml. Precipitate at 60°C. with an alcoholic 2 per cent oxine solution, until the supernatant liquid is orange-yellow. Heat to boiling and let the mixture stand on a hot plate for 30 minutes. Filter through a G4 sintered-glass crucible and wash with a warm, very dilute ammonia solution. Dissolve the precipitate in 3*N* hydrochloric acid and titrate according to the general procedure.

Note: Berg and Becker[235] use oxine for the determination of both thorium and cerium(III) in a mixture. The thorium is precipitated in an acetate buffer according to the procedure of Hecht and Ehrmann[236] and after filtration the cerium is determined in the way described above.

Indium: The composition of the indium precipitate with oxine is $In(C_9H_6ON)_3$.

Procedure:[237] To the test solution, which should be as free as possible of excess acid and contains 15–100 mg. of indium, add 2 g. of sodium acetate and 2 ml. of acetic acid. Dilute to 200 ml. with hot water, heat to 70–80°C., and add 5 per cent ethanolic oxine solution dropwise with stirring. Set aside for 2–3 hours and stir several times during cooling. Filter and wash with cold water. Dissolve the precipitate by heating in 10–15 per cent hydrochloric acid and titrate.

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[234] R. Berg, *Z. anal. Chem.*, 76, 191 (1929).

[235] R. Berg and E. Becker, *Z. anal. Chem.*, 119, 1 (1940).

[236] F. Hecht and W. Ehrmann, *Z. anal. Chem.*, 100, 98 (1935).

[237] W. Geilmann and F. W. Wrigge, *Z. anorg. Chem.*, 209, 129 (1932).

Note: If less than 15 mg. of indium is present, the precipitation volume and correspondingly the amounts of acetic acid and acetate added are reduced: for 5–15 mg., a volume of 100 ml. is satisfactory; for less than 5 mg., 50 ml. or less.

Gallium:[237,238] The precipitate of gallium with oxine is of similar composition to that of indium.

Procedure: Dilute the mineral acid solution of gallium to 100–200 ml. with water, add a slight excess of 5 per cent ethanolic oxine solution, and neutralize at 70–80°C. by dropwise addition of ammonia. (A slight excess of ammonia does no harm.) Heat the mixture on the water bath for 30–60 minutes with frequent stirring, cool, and allow to stand for 1–2 hours. Filter and wash first with about 20 ml. of warm water and then with cold water until the filtrate is colorless. Dissolve the precipitate in hydrochloric acid by heating for 10–15 minutes and titrate.

Note: Gallium is also quantitatively precipitated from ammoniacal tartrate solution. Geilmann and Wrigge[237] also give a method for the precipitation from strongly alkaline solution with neutralization to pH 6–8.

Lanthanum:[239] Dilute 10–20 ml. of the solution with 30–40 ml. of water, heat nearly to boiling, and add 5 ml. of 2*N* acetic acid and an excess of alcoholic 3 per cent oxine solution. (Acetic acid solution might be preferable.) Add 10 per cent ammonia solution dropwise until there is a strong smell of ammonia. Warm for 2–3 minutes in order to accelerate precipitation and filter after 1 hour. Dissolve the precipitate in 20–30 ml. of 2*N* hydrochloric acid and titrate.

Yttrium: Yttrium is precipitated quantitatively with oxine at pH 5–6 and may be determined bromometrically.[240] Thorium cannot be separated even by repeated reprecipitation.

Columbium: Süe[241] states that columbium may be precipitated as the oxinate and determined bromometrically or gravimetrically.

Zirconium: According to Balanescu,[242] the composition of the precipitate is strongly dependent on the conditions of precipitation and the nature of the solution. The following method gives a precipitate of formula $Zr(C_9H_6NO)_4$.

Procedure: To the solution add 10 ml. of nitric acid (sp. gr. 1.20), dilute to about 50 ml., evaporate to a volume of several milliliters, add another 5 ml. of nitric acid, and evaporate in the same way. Dilute to 50 ml., add 5–10 ml. of 3 per cent oxine solution and 50–70 ml. of 2*N* sodium or ammonium acetate. Stir, warm carefully, and keep boiling for some minutes. Allow to settle and filter. Wash with boiling water containing a little acetic acid, dissolve the precipitate in 50 ml. of 50 per cent sulfuric acid, and titrate in the usual way.

Note: Fairly good results are obtained with less than 12 mg. of zirconium

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[238] Cf. O. W. Rollins and C. K. Deischer, *Anal. Chem.*, 26, 769 (1954).

[239] T. I. Pirtea, *Z. anal. Chem.*, 107, 191 (1937).

[240] A. S. Murthy, T. P. Sarma, and B. S. V. R. Rao, *Z. anal. Chem.*, 145, 418 (1955).

[241] P. Süe, *Compt. rend.*, 196, 1022 (1933).

[242] G. Balanescu, *Z. anal. Chem.*, 101, 101 (1935).

(accuracy about 2–3 per cent); with larger amounts, the results are 5–6 per cent low.

6. Anthranilic Acid and Its Application to the Determination of Metals. This acid, $C_6H_4NH_2COOH$ (*o*-aminobenzoic acid), can be titrated by the Koppeschaar method;[243] 6 equivalents of bromine are consumed for each mole of acid. Funk and Ditt[244] titrate directly with bromide-bromate mixture and use a solution of 0.2 per cent indigo carmine and 0.2 per cent of styphnic acid as indicator. After the color change from green to yellow, the excess is back-titrated iodometrically. The solution should be at least 1.5N in hydrochloric acid at the end-point; otherwise the results are too low.

It has been shown[245] that better results can be obtained by tribromination of the anthranilic acid than by dibromination. An excess of bromate-bromide solution is added to the solution, which is more than 1.6N in hydrochloric acid. The mixture is set aside for 30 minutes and the excess is back-titrated iodometrically. The results are accurate to 0.5–1 per cent.

Funk and his coworkers have used this titration for the determination of various metals which are quantitatively precipitated, even at great dilution, in neutral or slightly acidic solution by sodium anthranilate. The precipitates have the composition $M(II)\cdot(C_7H_6O_2N)_2$.

Shennan, Smith, and Ward[245] found that the Funk and Ditt precipitation methods for the determination of zinc, cobalt, copper, and nickel gave good results. A small amount of acetate or tartrate should be added to buffer the solution, but large amounts[246] increase the solubility of the precipitate. Gotô[246] has studied the pH ranges for the quantitative precipitation of several metals.

Reagent: The technical acid is purified by recrystallization from water (with animal charcoal) and alcohol. A 3 per cent solution of the sodium salt is prepared by dissolving 3 g. in about 22 ml. of N sodium hydroxide. On testing with litmus paper, the solution should have a slightly acidic reaction. It is then filtered and diluted to 100 ml. When it is kept in the dark it is stable for 1 week.

Procedure. Zinc, Cadmium,[244] and Manganese:[247] Dilute the test solution, which should contain no free acid or at most very little acetic acid, to 150 ml. (80 ml. for Mn) for each 0.1 g. of metal. For each 0.1 g. of metal, add 25–30 ml. (60 ml. for Mn) of reagent at room temperature with constant stirring, set aside for 20 minutes (1 hour for manganese) and filter through a porcelain filter. Wash with a 0.2 per cent solution of the reagent and finally several times with alcohol. Dissolve the precipitate in 4N hydrochloric acid and titrate by the method described above.

Note: The determination of manganese in the presence of much calcium is unsatisfactory because of coprecipitation of calcium anthranilate.

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[243] A. R. Day and W. T. Taggart, *Ind. Eng. Chem.*, 20, 545 (1928).

[244] H. Funk and M. Ditt, *Z. anal. Chem.*, 91, 332 (1933).

[245] R. J. Shennan, J. H. F. Smith, and A. M. Ward, *Analyst*, 61, 395 (1936).

[246] H. Gotô, *J. Chem. Soc. Japan*, 55, 1156 (1934).

[247] H. Funk and M. Demmel, *Z. anal. Chem.*, 96, 385 (1934).

Cobalt, Nickel, and Copper: Funk and Ditt[248] found that these metals could be precipitated from neutral solution.

Procedure: Neutralize the solution (see zinc) and dilute with water if necessary to give 0.1 g. of cobalt or nickel or 0.05 g. of copper in 250–300 ml. of solution. Heat to boiling and precipitate with 35 ml. of the 3 per cent reagent solution for every 100 mg. of metal. Heat at gentle boiling for 5 minutes, set aside for 5–10 minutes, and filter. Proceed further as given for zinc and cadmium. For copper salts, back-titrate the slight excess of bromine with arsenious acid solution until the indicator turns green. One milliliter of 0.1*N* bromate corresponds to 0.737 mg. of cobalt, 0.734 mg. of nickel, or 0.795 mg. of copper.

Note: Nickel anthranilate is not very soluble in dilute hydrochloric acid; it is better to dissolve in hot concentrated acid and then to dilute.

Lead:[249]

Procedure: Dilute the neutral solution containing 0.1 g. of lead to 100 ml., add 30 ml. of a 3 per cent reagent solution, and set aside for at least 1 hour. Filter through a porcelain filter and wash with the reagent solution diluted 5–6 times. Dissolve the precipitate in hot 10 per cent ammonium acetate solution, add hydrochloric acid, cool thoroughly, and titrate.

Note: The accuracy of the method is about 1 per cent. Moderate amounts of alkali chloride or nitrate do not interfere but ammonium salts cause a negative error. The determination cannot be carried out in presence of acetate ions. Funk and Römer[249] obtained unsatisfactory results for the determination of mercury using the titrimetric finish.

7. Titrations with Bromine. Standard solutions of bromine can be used as titrants and have found occasional application. A detailed study of their use was made by Manchot and Oberhauser.[250] In a strong hydrochloric acid medium bromate-bromide solutions will serve the same purpose, but are said to work less smoothly and to give less distinct end-points. Bromine solutions can be used in alkaline and weakly acid media where bromate solutions are inapplicable.

The method of preparing the bromine solution depends on the particular determination for which it is to be used. Four main preparations have been described.

(1) An aqueous solution. This is very unstable and cannot be used at concentrations above 0.033*N*; it was used only by early investigators.

(2) A solution containing 20–22 per cent of hydrochloric acid. This is much more stable and 0.1*N* solutions may be prepared. Above a concentration of 24 per cent of hydrochloric acid the reaction does not go to completion.

(3) A solution 1*N* in potassium bromide. This solution is also moderately stable (see below).

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[248] H. Funk and M. Ditt, *Z. anal. Chem.*, **93**, 241 (1933).

[249] H. Funk and F. Römer, *Z. anal. Chem.*, **101**, 85 (1935).

[250] W. Manchot and F. Oberhauser, *Z. anorg. Chem.*, **130**, 161 (1923); **138**, 357 (1924); **139**, 40 (1924).

(4) A solution in glacial acetic acid which is used for the determination of iodine-bromine numbers.

The vapor pressure of bromine solutions decreases with increase in hydrochloric acid or bromide concentration.[250,251] The vapor pressure is 3 mm. in 20 per cent of hydrochloric acid, 1.7 mm. in N potassium bromide solution, and 0.26 mm. in glacial acetic acid.

For a discussion on the equilibria of bromine and potassium bromide in aqueous solution see the papers by Liebhafsky[252] and by Jones and Baeckström.[253]

The volatility of bromine is the main source of error, but the effect is minimized by titrating into small flasks with narrow necks, by adding hydrochloric acid or potassium bromide to the reaction mixture and, whenever possible, running the bromine into the test solution; the reverse titration should be avoided. A standard arsenite solution is sometimes used in conjunction with the bromine solution.

A 0.2 per cent solution of indigo carmine is to be preferred to methyl orange as indicator, but, when the solutions of bromine are aqueous, malachite green or crystal violet may be used. An indicator mixture of 0.2 per cent indigo carmine and styphnic acid has advantages for titration in colored solutions. In all cases, the indicator should only be added near the end of the titration.

In general, other titrants are to be preferred; accordingly, only a few of the methods will be described in detail. In addition to these, metallic dioxides,[254,255] antimony,[255] tin,[255] ferrous iron,[255,256] hydrogen peroxide,[255] chromate,[255,257] hypochlorite,[254,257] sulfide, sulfite,[255,257] nitrite,[255] phosphite, hypophosphite,[258] thiocyanate,[259] and ozone[260] can be determined by various direct and indirect procedures. Van der Meulen has studied the determination of urea, ammonia, formates,[261] mixtures of halogens and halates,[262] and selenium.[263] Aniline can be determined by bromination.[264]

[251] Cf. J. D'Ans and P. Höfer, *Z. angew. Chem.*, **47**, 71 (1934).

[252] H. A. Liebhafsky, *J. Am. Chem. Soc.*, **56**, 1500 (1934); **61**, 3513 (1938).

[253] G. Jones and S. Baeckström, *ibid.*, **56**, 1517 (1934).

[254] W. Manchot and F. Oberhauser, *Z. anorg. Chem.*, **130**, 161 (1923).

[255] *Idem, ibid.*, **139**, 40 (1924).

[256] *Idem, Z. anal. Chem.*, **67**, 196 (1926).

[257] *Idem, Ber.*, **57B**, 29 (1924).

[258] W. Manchot and F. Steinhäuser, *Z. anorg. Chem.*, **138**, 304 (1924).

[259] F. Oberhauser, *ibid.*, **144**, 257 (1925).

[260] W. Manchot and F. Oberhauser, *Z. anorg. Chem.*, **130**, 168 (1923).

[261] J. H. van der Meulen, *Chem. Weekblad*, **27**, 550 (1930).

[262] *Idem, ibid.*, **27**, 558, 578, 618 (1930); **28**, 82, 238, 258, 348 (1931).

[263] *Idem, ibid.*, **31**, 333 (1934).

[264] M. Francois, *J. pharm. chim.*, (6) **9**, 521 (1899); cf. A. V. Pamfilov, *Z. anal. Chem.*, **69**, 282 (1926); A. V. Pamfilov and V. E. Kisseleva, *ibid.*, **72**, 100 (1927); **75**, 87 (1928).

Arsenic: Manchot and Oberhauser[265] stated that bromine is to be preferred to iodine for the titration of arsenic(III) because the reducing effect of iodide in acid solution is avoided. The method is less attractive than others which are available (e.g., by iodate or bromate titration) and need not be considered further. The most important use of the titration is in the back-titration of bromine in procedures where this must be added in excess. For the determination of arsenical gases by titration with bromine see p. 568.

Ammonia: The determination of ammonia by oxidation with bromine has been studied frequently. Reference should be made to the discussion on p. 582. Manchot and Oberhauser[266] used a solution 0.1–0.2N in bromine and 1N in potassium bromide as reagent in the presence of twice the theoretical amount of 0.5N sodium hydroxide. When reaction was complete, the solution was acidified, treated with an excess of standard arsenite solution, and titrated with the bromine solution in the presence of indigo carmine as indicator. Levy[267] used a sodium bicarbonate medium to avoid side reactions.

Procedure: Transfer 0.006–0.020 g. of the ammonium salt to a flask fitted with a ground stopper, add 15 ml. of saturated sodium bicarbonate solution, and 0.067N bromine solution (120 g. of potassium bromide and 1.8 ml. of bromine dissolved in a liter of water) until the bromine color no longer fades. Add 4–5 ml. in excess. Stopper the flask and set aside for 5 minutes. Add 20 ml. of 5 per cent potassium iodide and 20 ml. of 2N sulfuric acid, taking care that no spray is lost owing to the reaction with bicarbonate. After 3–5 minutes titrate with 0.033N sodium thiosulfate solution, using starch indicator.

Notes: (1) The oxidation may be allowed to proceed for 5–30 minutes. It is quantitative at pH 8.

(2) Disodium hydrogen phosphate, borax, and sodium hydroxide (8–10 per cent solutions) were also used in place of bicarbonate. "After-blueing" was negligible with the first salt, slight with the second, and very pronounced with the last.

The method is applicable to the determination of nitrogen in organic compounds after decomposition by Kjeldahl's method. High results are obtained when iron is present. Tschepelewetzky and Posdniakowa[268] overcame this difficulty by the use of a phosphate buffer. They applied the method to the analysis of technical ammonium salts and to artificial manures.

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[265] W. Manchot and F. Oberhauser, *Z. anal. Chem.*, **130**, 161 (1923); *Z. anorg. Chem.*, 138, 357 (1924).

[266] W. Manchot and F. Oberhauser, *Ber.*, **57B**, 29 (1924).

[267] B. Levy, *Z. anal. Chem.*, 84, 98 (1931).

[268] M Tschepelewetzky and S. Posdniakowa, *Z. anal. Chem.*, **84**, **106** (1931).

Procedure: Transfer the sample and 10–15 ml. of concentrated sulfuric acid to a Kjeldahl flask. Heat gently to boiling for 30–50 minutes (until the solution clears and sulfur dioxide is no longer evolved). Dilute to the mark in a volumetric flask (to give approx. 0.05*N* ammonia solution). Take a 10–15 ml. aliquot, neutralize with the phosphate buffer (95 g. of disodium hydrogen phosphate and 5 g. of monosodium hydrogen phosphate per liter), and add 15 ml. in excess. Add an excess of 0.05*N* bromine solution (60 g. of potassium bromide and 2–4 ml. of bromine per liter). Stopper the container and set aside for 10 minutes. Add 20 ml. of 0.2*N* potassium iodide, 15 ml. of 20 per cent phosphoric acid, and titrate after 3 minutes with 0.02*N* sodium thiosulfate solution.

Carry out a blank determination on all reagents.

Formic Acid: The determination was studied by Oberhauser and Hensinger,[269] who described two methods, one based on direct oxidation of formic acid with bromine and the other on the reduction of mercuric chloride; the mercurous chloride formed was then determined bromometrically. Barium formate was used to standardize the bromine solution. A similar procedure was described by van der Meulen.[270]

Procedure: To 25 ml. of solution containing 35–40 mg. of formic acid add 50 ml. of water, 10 ml. of *N* potassium bicarbonate solution, and 10 ml. of 0.5*N* bromine in 10 per cent potassium bromide. Stopper the flask, set aside for 30 minutes, and add 10 ml. of *N* potassium iodide solution and 15 ml. of *N* hydrochloric acid. Titrate with standard thiosulfate.

Notes: (1) Borax may be used in place of bicarbonate.
(2) Oberhauser and Hensinger use standard arsenite in the back-titration.

Longstaff and Singer[271] state that the reaction rate is retarded in the presence of bromide and hydrogen ions owing to the formation of tribromide ions; the oxidation is between bromine molecules and formate.[272] They add pyridine to accelerate the reaction and to reduce the hydrogen-ion concentration.

Procedure: Transfer 5–10 ml. of the sample ($1–5 \times 10^{-4}$ mole of formic acid) to a narrow-necked flask (a 250 ml. graduated flask is suitable) containing 2.5 ml. of pyridine and add 20 ml. of bromine solution (Note 1). After 3 minutes add 10 ml. of potassium iodide solution and rinse the sides of the flask with 50 ml. of water. Add 5 ml. of 0.1*N* thiosulfate from a pipette and titrate the residual iodine with 0.04*N* thiosulfate in the usual way.

Notes: (1) The bromine solution is prepared by dissolving 2.9 ml. of bromine in 1 liter of glacial acetic acid and adding sufficient water to prevent the acid crystallizing. It is stored in a bottle fitted with a ground stopper and dispensed from an ordinary pipette which is filled by suction from a pump.

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[269] F. Oberhauser and W. Hensinger, *Z. anorg. Chem.*, 160, 366 (1927).

[270] J. H. van der Meulen, *Chem. Weekblad*, 27, 550 (1930).

[271] J. V. Longstaff and K. Singer, *Analyst*, 78, 491 (1953).

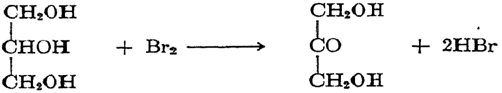
[272] Cf. O. L. Hammick, W. K. Hutchison, and F. R. Snell, *J. Chem. Soc.*, 127, 2715 (1925).

Pyridine is purified by distillation in the presence of 1 per cent bromine under reduced pressure. Very impure pyridine should be first distilled in the absence of bromine. The purified product is tested by running blanks on the bromine solution and pyridine for 1, 3, and 5 minutes. If these agree the product is sufficiently pure.

(2) For series analyses blanks should be run at the beginning and at the end, for the bromine titer may vary slightly.

(3) Nitrite may be determined in exactly the same way as formic acid.

Glycerin: According to Juhlin,[273] glycerin is oxidized by bromine in neutral solution:



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + Br_2 \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CO \\ | \\ CH_2OH \end{array} + 2HBr$$

Procedure: Transfer the solution containing 2–4 mg. of glycerin to a 500 ml. glass-stoppered Erlenmeyer flask and neutralize to methyl orange. Add 10 ml. of 0.1 per cent bromine water. Close the flask and allow to stand for 15 minutes (moisten the stopper with potassium iodide solution). Add 10 ml. of 10 per cent potassium iodide, dilute with 50–100 ml. of water, and titrate the liberated iodine with 0.02*N* thiosulfate. Simultaneously, run a blank on the bromine water used.

Mustard and Other War Gases: Mustard gas, Lewisite, and ethyl or phenyl dichloroarsine may be determined by titration with bromine.[274] One mole of bromine reacts with one mole of substance.

Procedure: Transfer 1–5 ml. of the solution (a $10^{-4}\,M$ solution of the gas in water or ethanol) to a 1.5 × 15 cm. test tube and add sufficient sulfuric acid to give a concentration of $0.1M$. Add a drop of methyl red and titrate with $10^{-4}M$ bromine solution until colorless. A comparison tube containing water should be used and both tubes should rest vertically on white paper; they should be viewed at an angle of 45° to the vertical.

Notes: (1) A $0.5M$ stock solution is prepared by shaking 50 ml. of *M* hydrochloric acid with 10 ml. of bromine. It is stored in a dark bottle in the presence of excess bromine. This solution is diluted to $10^{-4}M$ for the titration and is standardized against $10^{-4}M$ mustard gas, thiodiglycol, or iodometrically.

(2) The titrations are accurate to ±0.02 ml. of $10^{-4}\,M$ bromine per milliliter of final volume of solution. If the final volume is 10 ml., the end-point is sharp to ±0.02 ml. For larger amounts a more concentrated titrant should be used.

(3) Hydrogen sulfide and sulfides are the most likely interferences; hence the solutions must not be allowed to come in contact with rubber tubing or stoppers. Hydrogen sulfide absorbed from the air may be removed by boiling, but old solutions of sulfide cannot be freed from reducing substances in this way.

(4) Hypochlorite may be used as titrant in place of bromine. Although it is more stable, it reacts with many compounds to which bromine is inert.

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[273] O. Juhlin, *Z. anal. Chem.*, 113, 339 (1938).

[274] J. H. Northrop, *Proc. Soc. Exptl. Biol. Med.*, 67, 15 (1948).

Kurt Meyer Titration: Meyer[275] described a method for the determination of enolization and the equilibrium percentage of enol, based on bromine addition in an ethanolic medium. He determined the amount of combined bromine in various ways. For example, he titrated with ethanolic bromine to a permanent color or, after forming the bromoketone, he reacted this with iodide in acid solution and titrated the iodine formed. In the procedure generally recommended, however, an excess of standard ethanolic bromine is added, the excess is reacted with β-naphthol, and the bromoketone is determined iodometrically. The operation must be done rapidly to avoid the keto changing to the enol form.

Cooper and Barnes[276] used a methanolic solution and preferred diisobutylene to β-naphthol to remove excess of bromine. Gero[277] recommended the replacement of bromine with iodine monochloride which, he states, combines more rapidly.

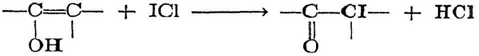
Procedure: Dissolve 1–1.5 g. of acetoacetic ester in 30 ml. of ethanol, cool to −7°C., add 0.1 or $0.2N$ ethanolic bromine until a yellow-brown color is obtained, and immediately introduce 2 ml. of 10 per cent β-naphthol. Add potassium iodide, warm, and titrate with $0.1N$ thiosulfate.

Notes: (1) The whole operation up to destroying the excess of bromine should not occupy more than 15 seconds.

(2) The error is 0.1–0.2 per cent.

(3) The method did not give satisfactory results for acetyl dibenzoylmethane and diacetylacetone.

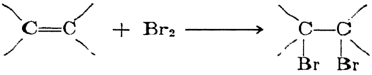
(4) Gero[277] mixes 0.1 millimole of the substance with 0.1 millimole of dry sodium bicarbonate and 0.1 millimole of $2.5N$ iodine monochloride in methanol. He then adds immediately 2–3 ml. of 15 per cent sodium iodide and titrates the liberated iodine with thiosulfate.



$$\underset{\displaystyle\mathrm{OH}}{\underset{|}{-\mathrm{C}}}{=}\underset{|}{\mathrm{C}}- + \mathrm{ICl} \longrightarrow \underset{\displaystyle\mathrm{O}}{\underset{\|}{-\mathrm{C}}}-\underset{|}{\mathrm{CI}}- + \mathrm{HCl}$$

8. Determination of Double Bonds.

Bromine adds rapidly to double bonds:



Unfortunately in the treatment of many unsaturated compounds, side reactions (substitution, hydrolysis) interfere with the simple addition reaction: it is beyond the scope of this book to discuss these side reactions. Reference should be made to a recent review article[278] which gives a complete, critical survey of the subject with experimental details.

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[275] K. H. Meyer, *Liebigs Ann.*, **380**, 212 (1911); K. H. Meyer and P. Kappelmeier, *Ber.*, **44**, 2718 (1911); K. H. Meyer, *ibid.*, 2725; cf. H. P. Kaufmann, *ibid.*, **55**, 2255 (1922); H. P. Kaufmann and G. Wolff, *ibid.*, **56**, 2521 (1923); G. Schwarzenbach and E. Felder, *Helv. Chim. Acta*, **27**, 1044 (1944).

[276] S. R. Cooper and R. P. Barnes, *Ind. Eng. Chem., Anal. Ed.*, **10**, 379 (1938).

[277] A. Gero, *J. Org. Chem.*, **19**, 469 (1954); *Anal. Chem.*, **26**, 609 (1954).

Solutions of bromine and of bromate-bromide mixture have been widely used for the determination of unsaturation. Pyridine dibromide has been suggested as a reagent for mild bromination reactions;[279] the reaction time is shorter than with bromine. If there are no interfering side reactions, the titrations may be made directly or by adding an excess of reagent and back-titrating. Styrene, for example, reacts smoothly to give dibromostyrene and can be titrated directly.

Quinine Alkaloids: Quinine alkaloids which contain the vinyl group can be titrated with bromate. Schulek and Kovács[280] give a procedure for the determination of quinine, quinidine, cinchonine, cinchonidine, and cupreine.

Procedure: Dissolve a sample of the compound containing 0.1–0.2 g. of quinine alkaloid in 10 ml. of water; if necessary, add some hydrochloric acid. Add 20 ml. of 20 per cent hydrochloric acid, 1 g. of potassium bromide, and 1 drop of 0.2 per cent ethanolic *p*-ethoxychrysoidine solution. Titrate carefully with $0.1N$ bromate until the red color disappears. To ensure that the solution has not been overtitrated, add 50 ml. of water and 0.2 g. of potassium iodide and titrate the liberated iodine with $0.1N$ thiosulfate. The amount of thiosulfate is deducted from the amount of bromate used. One milliliter of $0.1N$ bromate corresponds to 16.216 mg. of water-free quinine or quinidine, 14.715 mg. of cinchonine or cinchonidine, and 15.515 mg. of cupreine.

Note: The cupreine derivatives optochine, eucupine, and vucine (isooctyldihydrocupreine) do not interfere markedly; 0.3 g. of eucupine or vucine consumes 0.12 or 0.17 ml. of $0.1N$ bromate, respectively, but this amount can be back-titrated iodometrically.

Acrylic Esters: Albertson and MacGregor[281] determined monomer in partly polymerized acrylic and allyl esters by brominating with an excess of bromate-bromide mixture; about twice the theoretical amount should be used. The method is applicable only to pyridine-soluble polymers.

Procedure. Acrylic Esters: Dissolve 0.04–0.05 g. of sample in 25 ml. of pyridine. Add a 5 ml. aliquot dropwise to 20 ml. of 0.025–0.05 N bromate solution containing bromide in a 250 ml. flask fitted with a ground-in stopper; a fine suspension of the polymer is obtained. Acidify with 70 ml. of 10 per cent sulfuric acid and set aside in the dark for 20 minutes at 20–25°C. Add 10 ml. of carbon tetrachloride to dissolve the polymer, 1 ml. of 30 per cent potassium iodide solution, and titrate immediately with $0.05N$ thiosulfate; starch is added as indicator.

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[278] A. Polgár and J. L. Jungnickel, in *Organic Analysis*, Vol. III, Interscience Publishers, New York-London, 1956.

[279] K. W. Rosenmund and W. Kuhnhenn, *Z. Nahr. Genussm.*, 46, 154 (1923); cf. *Chem. Eng. News*, 1948, 1238.

[280] E. Schulek and J. Kovács, *Z. anal. Chem.*, 121, 21 (1941).

[281] C. E. Albertson and I. R. MacGregor, *Anal. Chem.*, 22, 806 (1950).

Allyl Esters: Proceed as above but set aside for only 10–15 minutes at 0°C.; otherwise bromine substitution takes place because allyl esters are more reactive then acrylic esters.

$$\text{Per cent unsaturation in polymer} = S = \frac{(A - B) \times M \times 50}{W \times 0.2E}$$

S = per cent monomer, A = number of equivalents of bromine, B = number of equivalents of thiosulfate, M = mol. wt., W = sample wt. (g.), and E = number of double bonds in the monomer.

For the determination of bromine numbers of fats and oils the appropriate textbooks of applied chemistry should be consulted for the necessary details. Some of the more important work in this field is covered in papers by Winkler and several later investigators.[282]

Francis[283] gave a survey of the older literature and described a procedure for the determination of the unsaturated content of petroleum products. Further details of the determination of olefinic unsaturation may be found in the review by Polgár and Jungnickel.[278]

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[282] L. W. Winkler, *Z. Nahr. Genussm.*, **43**, 201 (1922); *Pharm. Zentralhalle*, **68**, 433 (1927); *Arch. Pharm.*, **265**, 554 (1927); **266**, 189, (1928); *Z. anal. Chem.*, **93**, 172 (1933); W. Manchot and F. Oberhauser, *Z. Nahr. Genussm.*, **47**, 261 (1924); H. P. Kaufmann, *Z. Untersuch. Lebensm.*, **51**, 3 (1926); E. Rupp and W. Brachmann, *Z. anal. Chem.*, **68**, 155 (1926); K. Uhrig and H. Levin, *Ind. Eng. Chem., Anal. Ed.*, **13**, 90 (1941).

[283] A. W. Francis, *Ind. Eng. Chem.*, **18**, 821 (1926).

CHAPTER XIII

OXIDATION WITH HYPOHALITES

1. **General Considerations.** The assay of hypochlorites by direct titration of sodium arsenite as described by Gay-Lussac[1] is one of the earliest of titrimetric methods, but the use of hypochlorite as a *titrant* is of more recent date. It is of interest to note that the latest methods bear a remarkable resemblance to that early method of Gay-Lussac, who assayed hypochlorite by running the solution into a known amount of sodium arsenite solution, in the presence of indigo, and detected the end-point by the bleaching of the dyestuff.

Methods using hypobromite for the determination of ammonia and urea were described in the last century. Plehn[2] determined urea by titrating directly with sodium hypobromite until evolution of nitrogen ceased. Quinquaud[3] added an excess of standard hypobromite, destroyed this with a standard arsenite solution, and then titrated with more of the hypobromite solution in the presence of indigo as irreversible indicator. Krocker and Dietrich[4] determined ammonia and nitrate (after reduction to ammonia) by adding an excess of a standard solution of "brominated sodium hypochlorite" and back-titrating with standard arsenite solution, using starch-iodide paper as external indicator.

Hypochlorite as a titrant appears to have been used first by Fordos and Gelis;[5] they titrated thiosulfate and various polythionic acids. The end-point was determined by the bleaching of indigo or when "the smell of chlorine appeared." These investigators suggested that arsenite, antimonite, and the lower phosphorus acids might also be determined similarly.

The use of hypochlorite as a *general* titrant does not appear to have been proposed until 1924, when Jellinek and Kresteff[6] examined its application to a number of determinations. The use of hypochlorite was extended as a result of the investigations of Kolthoff and Stenger.[7] They recommended calcium hypochlorite because of its greater stability, and the addition of potassium bromide to the solution being titrated so that in effect the titrant behaved like a standard solution of hypobromite. As an alternative to the iodometric determination of the excess of hypochlorite, they also recommended the addition of an excess of a standard arsenite solution and direct titration of the excess with hypochlorite using bordeaux as an irreversible indicator.

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[1] J. L. Gay-Lussac, *Ann. chim. et phys.*, (2) 60, 225 (1835).

[2] F. Plehn, *Ber.*, 8, 582 (1875).

[3] E. Quinquaud, *Monit. sci.*, (3) 11, 641; *Z. anal. Chem.*, 21, 605 (1882).

[4] Krocker and E. Dietrich, *Z. anal. Chem.*, 3, 64 (1864).

[5] J. Fordos and A. Gelis, *Ann. chim. et phys.*, (3) 22, 60, 66 (1848).

[6] K. Jellinek and W. Kresteff, *Z. anorg. Chem.*, 137, 333 (1924).

The possibility of using sodium hypobromite and hypochlorite for direct titration was examined by Tomíček and his coworkers.[8] They pointed out that solutions prepared by the addition of bromine to a solution of sodium hydroxide must inevitably contain some bromate and bromide, and possibly a trace of bromite.

$$Br_2 + 2NaOH \longrightarrow NaBrO + NaBr + H_2O \quad (1)$$

$$3NaBrO \longrightarrow 2NaBr + NaBrO_3 \quad (2)$$

To a lesser degree there is decomposition according to

$$2NaBrO \longrightarrow 2NaBr + O_2 \quad (3)$$

The iodometric titration determines the sum of the hypobromite and bromate present, whereas the arsenite titration determines only hypobromite. Accordingly, Tomíček and Jašek were able to determine the amount of bromate present by the difference in titer obtained between the two procedures (using a potentiometric end-point in the arsenite titration) and they were able to establish the optimum alkali concentration as being 0.5 N. At higher concentrations the bromate concentration becomes appreciable and at lower concentration (0.25 N) the oxidizing properties deteriorate rapidly.

Tomíček *et al.* emphasized also that the hypobromite solution should be prepared with ice-cooling; it should be stored in the dark and should be standardized before each series of titrations. The alkalinity at the end of the titration with arsenite should be about 1.5N.

When ammonium salts, thiocyanate, and thiosulfate are titrated directly with hypobromite the errors are about 3 per cent high. When calcium hypochlorite is used as titrant and potassium bromide is added to the solution being titrated, these errors no longer occur.

[7] I. M. Kolthoff and V. A. Stenger, *Ind. Eng. Chem., Anal. Ed.,* 7, 79 (1935).

[8] O. Tomíček and M. Jašek, *Collection Czech Chem. Communs.,* 10, 353 (1938); O. Tomíček and P. Filipovič, *ibid.*, 340, 415.

This effect is due to the presence of bromate which is formed when hypobromite solutions are prepared and when they are stored (see equation 2), for the addition of bromate to calcium hypochlorite solutions produces the same effect. The mechanism of the reaction is not certain. Kolthoff and Laur[9] had confirmed that some ammonia is transformed to oxides of nitrogen during the oxidation, and Tomíček *et al.*[8] agree that this explanation is a possibility. However, no similar explanation can account for the reaction with thiosulfate where the final product is sulfate; hence it is suggested that bromate induces or catalyzes some reactions which cause decomposition of hypobromite during the titration. Although chlorate is undoubtedly present in solutions of calcium hypochlorite, it has no effect on the oxidizing properties, as can be shown by adding further amounts of chlorate. When a titration is made with a solution containing added amounts of chlorite, the chlorite decomposes, the test solution becomes yellowish green, and low results are obtained.

When ammonia is titrated with calcium hypochlorite without the addition of bromide, high results are obtained. This effect can also be ascribed to further oxidation to nitrogen oxides.

From the foregoing discussion it can be concluded that:

1. Titration with hypochlorites without the addition of bromide, and with hypobromites prepared from bromine and alkali can give rise to significant errors.
2. The best results are obtained by using a standard solution of hypochlorite (which is far more stable than hypobromite) and adding bromide to the test solution.
3. There are many contradictory statements in the literature and some of the titrations do not appear to be stoichiometric. Further systematic critical studies in this field are desirable.

The oxidation potentials of the chloride-hypochlorite system in acid and alkaline solutions are as follows:[10,11]

$$H_2O + Cl^- = HClO + H^+ + 2e \qquad E^\circ = +1.49$$

$$2OH^- + Cl^- = ClO^- + H_2O + 2e \qquad E^\circ_B = +0.89$$

In acid solution the couple has no chemical meaning, for chloride and hypochlorite react to produce chlorine:

$$Cl^- + HClO + H^+ = Cl_2 + H_2O$$

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[9] I. M. Kolthoff and A. Laur, *Z. anal. Chem.*, **73**, 177 (1928).

[10] W. M. Latimer, *Oxidation Potentials*, Prentice-Hall, New York, 1952.

[11] The European sign convention is used as elsewhere in this book.

Therefore it would be of more significance to consider the potential as that of the chlorine-chloride system:

$$2Cl^- = Cl_2 + 2e \qquad E^0 = +1.3583$$

The potentials of the bromide-hypobromite system are as follows:

$$H_2O + Br^- = HBrO + 2H^+ + e \qquad E^\circ = +1.33$$

$$2OH^- + Br^- = BrO^- + H_2O + 2e \qquad E_B^0 = +0.76$$

Detection of the End-Point: The method which has been most generally used for detecting the end-point consists of adding a measured excess of hypochlorite or hypobromite to the substance being determined, and titrating the unconsumed oxidant iodometrically after acidification. Gay-Lussac's use of indigo has already been mentioned; when assaying hypochlorite he also titrated into a known amount of mercurous chloride (produced *in situ*) until the precipitate just disappeared. Kolthoff and Stenger[7] found that the usual redox indicators were unsuitable. They examined several dyestuffs as irreversible indicators and concluded that bordeaux was the best; they also used the iodometric method. Other irreversible indicators which have been recommended are cresyl violet,[12] brasilin and santolin,[13] cochineal,[14] and amaranth (*C.I.* 184).[15] Teorell[16] titrates excess of hypobromite with a standard solution of naphthyl red (benzolazo-α-naphthylamine) until no further bleaching is obtained.

In their titrations with sodium hypochlorite in a slightly acid medium, Jellinek and Kresteff[6] used potassium iodide or bromide, indigo, methyl red, methyl orange, or aniline hydrochloride as indicator. They considered that potassium bromide was best; at the end-point the yellow color of bromine appears. In a later paper, however, Jellinek and Kühn[17] preferred potassium iodide and starch.

Willard and Manalo[18] examined several derivatives of diphenylamine in direct titrations with sodium hypobromite and found that satisfactory end-points were obtained with diphenylaminesulfonic acid and aminodiphenylaminesulfonic acid. The former indicator gives a reversible change, but the latter, although destroyed at the end-point, gives a more distinct change and a smaller blank value.

[12] O. G. Sheintsis, *Zavodskaya Lab.*, **12**, 930 (1946).

[13] J. Bitskei and K. Petrich, *Magyar Kém. Lapja*, 2, 230 (1947).

[14] J. Bitskei and M. Forhencz, *ibid.*, 117.

[15] R. Belcher, *Anal. Chim. Acta*, **4**, 468 (1950).

[16] T. Teorell, *Biochem. Z.*, **248**, 246 (1932).

[17] K. Jellinek and W. Kühn, *Z. anorg. Chem.*, **138**, 99 (1924).

[18] H. H. Willard and G. D. Manalo, *Ind. Eng. Chem., Anal Ed.*, **19**, 167 (1947).

Erdey and Buzás[19] have recently proposed the use of a 0.01 per cent solution of luminol dissolved in 0.005*N* sodium hydroxide as a chemiluminescent indicator for titrations with hypochlorite or hypobromite. For titration with hypochlorite, the test solutions are heated to 80°C. and 10 ml. of indicator is used. The titrations are done at room temperature with hypobromite; 3 ml. of indicator is sufficient. The end-point is marked by an intense luminescence which persists for several seconds; further additions of titrant should not give any further luminescence. Several substances were determined; in most cases the titrations were done in a sodium hydroxide solution.

Sinn found that quinoline yellow could be used as an internal indicator in the assay of hypochlorite.[20] He titrated a standard arsenite solution containing potassium bromide with the solution of hypochlorite. The change was reversible. Young and Das Gupta[21] were unable to confirm these results but their conditions were criticized adversely by Belcher,[22] who examined quinoline yellow as indicator for the titration of arsenite with a standard solution of sodium hypochlorite. The indicator gave sharp reversible end-points (yellow-green to colorless) in direct titrations in the presence of bromide. In the presence of bicarbonate, however, the color change was poor, and when bromide was not added the indicator was destroyed at the end-point.

Belcher[15] showed that tartrazine is a good reversible indicator in the titration of arsenite with sodium hypochlorite in a bicarbonate medium. It is necessary to have bromide present; otherwise the indicator is destroyed at the end-point. The change is from yellow to colorless. Several other pyrazolone dyestuffs were examined, but only the yellow dyestuffs gave reversible color changes and none was as good as tartrazine. This indicator is also used in the determination of nitrogen in organic compounds after decomposition by Kjeldahl's method (p. 584). Clark[23] has applied it in a submicro method in which the excess of hypobromite is titrated with a standard solution of the dyestuff; the end-point is detected spectrophotometrically.

Potentiometric[8] and amperometric[24] methods for detection of the end-point have been used.

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[19] L. Erdey and I. Buzás, *Acta Chim. Acad. Sci. Hung.*, 6, 93, 115 (1955).

[20] V. Sinn, *Chim. anal.*, 29, 58 (1947).

[21] J. H. Young and R. N. Das Gupta, *Analyst*, 74, 367 (1949).

[22] R. Belcher, *Anal. Chim. Acta*, 5, 27 (1951).

[23] S. J. Clark, *Chem. Age*, 74, 24 (1956).

[24] I. M. Kolthoff, W. Stricks, and L. Morren, *Analyst*, 78, 405 (1953); H. A. Laitinen and D. E. Woerner, *Anal. Chem.*, 27, 214 (1955).

The indicators recommended by the authors are given in Table I. Blanks should be determined for each batch of indicator because they may vary considerably.

TABLE I

C.I. No.	Indicator	Stock solution (aqueous) (per cent)	Color change	Reversibility	Amt. per titration (in drops)
88	Bordeaux	0.2	Pink–colorless	Irreversible	1–2
801	Quinoline yellow	0.2	Yellow–colorless	Reversible	10
640	Tartrazine	0.2	Yellow–colorless	Reversible	10

Stability of Solutions: Many investigators have studied the kinetics of the decomposition of hypobromite and hypochlorite.[25]

The reactions involved when hypobromite is prepared from bromine and sodium hydroxide have been considered (p. 574). The first reaction is immediate and quantitative; the second and third are dependent on temperature, light, and alkalinity. Dehn[26] considers that the best method of preparation is to place a solution of sodium hydroxide in the lower part of a desiccator and to place a vessel containing bromine in the upper part. The reaction then proceeds slowly according to the spontaneous evaporation of bromine. This yields a solution containing about 50 per cent of the bromine as hypobromite, whereas by the usual methods only about 40 per cent is obtained as hypobromite. However, this method is too tedious for general use.

The decomposition of hypobromite is accelerated by a number of substances. Fleury[27] noted that traces of nickel, cobalt, and copper salts have a profound effect; traces of metal oxides[9] and charcoal[28] behave similarly. Erdey and Buzás[29] remove heavy metals by adding $1M$ magnesium chloride solution (20 ml. per liter of $0.1N$ hypochlorite); the hydroxides precipitate with magnesium hydroxide. The solution is shaken thoroughly and, after 24 hours, is filtered through a sintered-glass filter.

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[25] H. Kretzschmar, *Z. Elektrochem.*, **10**, 789 (1904); A. Skrabal, *Monatsh.* **28**, 319 (1907); **30**, 51 (1909); J. Clarens, *Compt. rend.*, **157**, 216 (1913); F. Foerster and P. Dolch, *Z. Elektrochem.*, **23**, 137 (1917); A. J. Allmand, P. W. Cunliffe, and R. E. W. Maddison, *J. Chem. Soc.*, **1927**, 655; J. J. Weiss, *Z. Elektrochem.*, **37**, 20, 271 (1931); *Z. anorg. Chem.*, **192**, 97 (1930); C. F. Prutton and S. H. Maron, *J. Am. Chem. Soc.*, **57**, 1652 (1935); F. Pollak and E. Doktor, *Z. anorg. Chem.*, **196**, 89 (1931); H. A. Liebhafsky and B. Makower, *J. Phys. Chem.*, **37**, 1037 (1933); R. M. Chapin, *J. Am. Chem. Soc.*, **56**, 2211 (1934); R. H. Betts and A. N. Mackenzie, *Can. J. Chem.*, **29**, 666 (1951).

[26] W. M. Dehn, *J. Am. Chem. Soc.*, **31**, 525 (1909).

[27] P. Fleury, *Compt. rend.*, **171**, 957 (1920).

[28] I. M. Kolthoff, *Rec. trav. chim.*, **48**, 291 (1929).

Jellinek and Kresteff[6] found that a $0.1N$ solution of sodium hypochlorite in sodium hydroxide remained unchanged over 7 days when kept in a clear glass bottle. After 17 days the titer had decreased by 1.5 per cent. Bitskei[30] states that a $0.1N$ solution showed practically no decomposition if kept in a dark bottle or in a Winkler burette covered with opaque material.

The optimum pH for maximum stability is 12.5 according to Goldstone and Jacobs.[31] They claimed that a $0.005N$ solution was stable for 2–3 months when stored in a dark bottle at this pH. The loss in titer of a $0.1N$ solution of calcium hypochlorite which had been stored in the dark for 3 months was 0.5–1 per cent.[7] A $0.01N$ solution was less stable but could be kept for several days without significant loss in titer if stored in the dark. Similar results were reported by Tomíček and Filipovič.[8]

Preparation and Standardization of Solutions: Oxidation by means of hypochlorite or hypobromite may be formulated

$$ClO^- + H_2O + 2e \longrightarrow Cl^- + 2OH^-$$

hence a normal solution of sodium hypochlorite or hypobromite is $0.5\,M$ and a normal solution of calcium hypochlorite is $0.25M$.

0.1N Calcium Hypochlorite: Add 6–10 g. (depending on the amount of available chlorine) to 250 ml. of distilled water, shake, and filter on a Buchner funnel to remove iron oxide and other insoluble constituents. Dilute to 1 liter and store in a bottle painted black on the outside.

An analysis of a solution prepared as above from a sample obtained from the Mathieson Alkali Co., Niagara Falls, N.Y., had the following composition

ClO^-	$0.1068\,N$	OH^-	$0.0037\,N$
Ca^{2+}	$0.0743\,N$	Cl^-	$0.0478\,N$
Na^+	$0.0306\,N$		

This corresponds to: $Ca(OCl)_2$, $0.0267M$; $Ca(OH)_2$, $0.0019M$; $CaCl_2$, $0.0068M$, and NaCl, $0.0306M$.

A turbidity due to calcium carbonate forms after a time but this has no harmful effect.

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[29] L. Erdey and I. Buzás, *Acta. Chim. Acad. Sci. Hung.*, 6, 115 (1955).

[30] J. Bitskei, *Magyar Kém. Folyóirat*, 50, 97 (1944).

[31] N. I. Goldstone and M. B. Jacobs, *Ind. Eng. Chem., Anal. Ed.*, 16, 206 (1944).

0.1N Sodium Hypochlorite: Dilute bromine-free sodium hypochlorite according to its assay (p. 263) to give an approximately 0.1*N* solution. Store in a dark bottle. If the alkali content is required this may be determined as follows.

Procedure:[32] To 10 ml. of the concentrated solution add 30 ml. of 20 volume hydrogen peroxide (neutralized to phenolphthalein) together with 5 ml. of neutral 0.5*M* barium chloride solution. Add 1 ml. of phenolphthalein indicator and titrate with 0.1*N* hydrochloric acid.

Some investigators prefer to prepare the solution by passing chlorine into alkali, and others to use various commercial preparations sold for household use.[22,31,33]

0.1N Sodium Hypobromite: Dissolve 24 g. of pure sodium hydroxide in 1 liter of distilled water and cool to −4°C. in a mixture of ice and salt. Add 8 g. of pure bromine. Shake thoroughly and leave the solution in the cooling mixture for 2 hours. Standardize after 12 hours.

Note: This preparation is that of Tomíček and Jašek[8] and appears to be the most stable solution which has been proposed. They standardized the solution iodometrically or potentiometrically with sodium arsenite as titrant but preferred the latter procedure (p. 574). Although they describe the successful determination of several substances, potentiometric titration was used in all cases. Several other preparations have been described and are included in some instances at the appropriate points in the text.

Standardization of 0.1N Hypochlorite: Solutions of hypochlorite should be restandardized every 4–5 days as a precautionary measure; solutions of hypobromite should be standardized immediately before use (see note 3).

Procedure (a). With a Solution of Standard Sodium Thiosulfate: To 25 ml. of hypochlorite solution add 1–1.5 g. of potassium iodide and 5 ml. of 6*N* sulfuric acid. Titrate the liberated iodine with standard sodium thiosulfate solution in the usual way.

Procedure (b). With a Solution of Standard Sodium Arsenite: Transfer 25 ml. of 0.1*N* sodium arsenite solution to a 250 ml. Erlenmeyer flask, add 1 g. of potassium bromide and 0.5 g. of sodium bicarbonate. Swirl the contents of the flask until the solids have dissolved. Titrate with the hypochlorite solution until within a few milliliters of the expected end-point, add 1 drop of aqueous 0.2 per cent bordeaux indicator (*C.I.* 88) and continue the titration dropwise with constant shaking until the pink color fades. Add 1 more drop of indicator and, if the color does not fade, continue the titration until the color changes from pink to colorless or light yellow-green. Subtract the indicator blank (Note 1) and calculate the normality of the hypochlorite solution.

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[32] J. Haslam and G. Moses, *Analyst*, **75**, 346 (1950); cf. E. Rupp and F. Lewy, *Z. anal. Chem.*, **73**, 283 (1928).

[33] J. L. Leitch, *J. Franklin Inst.*, **239**, 334 (1945).

Notes: (1) The indicator correction is 0.03 ml. of $0.1N$ hypochlorite for each 0.1 ml. of indicator in a final volume of 50–75 ml. If there is any doubt that the end-point has been reached and that the color change is due to premature bleaching, add a further drop of indicator.

(2) The reversible indicators tartrazine or quinoline yellow may be used instead of bordeaux. Proceed exactly as above but add 10 drops of 0.05 per cent tartrazine. The yellow color changes to colorless at the end-point. When a drop or so more arsenite is added the color returns slowly and the solution may be retitrated. The return of color is accelerated by adding more arsenite (1–2 ml.). The indicator correction varies somewhat with each batch of dyestuff. A typical blank is 0.05 ml. of $0.05N$ hypochlorite for 10 drops of indicator.

If the approximate end-point is not known, add 5 drops of indicator at the start of the titration and a further 5 drops when the color has almost faded.

Proceed in the same way with quinoline yellow as indicator but omit the addition of sodium bicarbonate and use 10 drops of a 0.2 per cent aqueous solution. The color change is also from yellow to colorless and reverses when more arsenite is added.

The indicator correction is also variable with different batches, as is the intensity of color; in some cases the correction is negligible.

(3) Sodium hypochlorite or calcium hypochlorite is standardized in exactly the same way. Either method may be used.

Sodium hypobromite is usually standardized by the iodometric method for general purposes, but in certain cases it may be necessary to standardize against a pure sample of the substance being determined. Details will be given later at the appropriate part of the text.

(4) The arsenite method may be operated in the presence of iron(III), chromate, or arsenate. (See also the observations of Tomíček *et al.*, p. 574.) The presence of iodide causes errors in the arsenite procedure but has no effect in the iodometric procedure.

2. Determination of Inorganic Compounds. *Arsenic:* The determination of arsenic (as arsenite) has already been considered in the standardization of hypochlorite (p. 580).

Jellinek and Kresteff[6] titrated in a slightly acid medium at 40–50° C. with starch and potassium iodide as indicator, or at room temperature with potassium bromide as indicator. The results were high in both cases but reproducible; hence an empirical standardization was recommended. Their procedure is less satisfactory than that described on p. 580 and need not be considered further. Erdey and Buzás[19] add 10–30 ml. of N sodium hydroxide solution and 10 ml. of luminol indicator (p. 577), dilute to 100 ml., and titrate at 80° C. with $0.1N$ sodium hypochlorite until the luminescence persists for 2 minutes. Hypobromite may also be used.

For the determination of small amounts of arsenic (0.1–1 mg.) Goldstone and Jacobs[31] used the following method.

Procedure: To 4–5 ml. of the arsenite solution (*ca.* $0.005N$) add 5 ml. of concentrated hydrochloric acid and dilute to 35–40 ml. Add 1 drop of 0.05

per cent methyl orange and titrate with sodium hypochlorite, adding a further drop of indicator near the end-point. Run a blank on all the reagents.

Notes: (1) The sodium hypochlorite solution is prepared by diluting 8 ml. of a commercial solution (5 per cent available chlorine) to approximately 2 liters in a brown glass bottle. If necessary the pH is adjusted to 12.5 by adding sodium hydroxide (1 g.).

(2) When the titration is carried out in acid medium, it is preferable to use potassium bromate as titrant because this solution can be kept indefinitely without change in titer (p. 506).

Antimony: Jellinek and Kresteff[6] determined antimony(III) by a procedure similar to the one they recommended for arsenic(III). The same difficulties were encountered. Goldstone and Jacobs[31] determined small amounts of antimony (0.1–1 mg.) in exactly the same way as arsenic(III) (above). Erdey and Buzás[19] determine antimony as in their method for arsenic(III) but add 1 g. of sodium potassium tartrate.

Tin: Jellinek and Kresteff[6] titrated tin(II) directly with sodium hypochlorite under an atmosphere of carbon dioxide. With potassium iodide and starch as indicator they obtained an overconsumption of titrant because of the presence of chlorate, which reacted in the iodometric standardization, but only slowly in the hypochlorite titration. Accordingly, they recommend that the hypochlorite solution should be standardized against a standard solution of tin(II). Potassium bromide (p. 576) is to be preferred as indicator.

The titration was applied to the determination of tin in white metal. The original paper should be consulted for details.

Chromium: Chromium(III) is oxidized by hypobromite:

$$2Cr^{3+} + 3OBr^- + 5H_2O \longrightarrow 2CrO_4^{2-} + 3Br^- + 10H^+$$

Erdey and Buzás[34] determine chromium(III) by adding an excess of hypobromite and back-titrating with hydrogen peroxide (p. 650). Lucigenin (p. 650) is used as indicator. Chromium(III) may be determined in the presence of chromate in this way.

Procedure: To the neutral solution of chromium(III) add 10 ml. of $1N$ sodium hydroxide and a known excess of $0.1N$ sodium hypobromite. After 5 minutes add 1 ml. of 0.5 per cent lucigenin per 100 ml. of solution and back-titrate with standard hydrogen peroxide.

The hypobromite solution is standardized against the hydrogen peroxide in the same way.

Ammonia: The determination of ammonia by oxidation with hypobromite was restudied by several investigators after the turn of the century.[35] It was observed that oxidation was not straightforward and could go in part beyond the formation of nitrogen to yield oxides of nitrogen (p. 574). Hypochlorite produces even more oxides of nitrogen than hypobromite.[36]

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[34] L. Erdey and I. Buzás, *Acta. Chim. Acad. Sci. Hung.*, **6**, 77 (1955).

[35] E. Rupp and E. Rossler, *Arch. Pharm.*, **243**, 104 (1905); P. Artmann and A. Skrabal, *Z. anal. Chem.*, **46**, 5 (1907); N. Schilow, *Z. physik. Chem.*, **42**, 5 (1903); D. R. Nanji and W. S. Shaw, *Analyst*, **48**, 473 (1923); M. B. Donald, *ibid.*, **49**, 375 (1924).

A systematic study of the reaction between ammonia and hypobromite was made by Kolthoff and Laur.[9] They concluded that the reaction was not quantitative because of nitrogen oxide formation; "after-blueing" occurred and it was necessary to allow the oxidation to proceed for some little time. Nevertheless under controlled conditions, satisfactory results could be obtained.

Procedure: To 25 ml. of solution contained in a flask fitted with a ground stopper, add 25 ml. of water, 10 ml. of $1N$ potassium bicarbonate, and 10 ml. of hypobromite solution (Note 1). Stopper the flask, mix, and set aside for 30 minutes. Add 10 ml. of N potassium iodide solution and 15 ml. of N hydrochloric acid. Stopper the flask and set aside for 10–15 minutes. Titrate the excess of hypobromite with standard thiosulfate solution.

Notes: (1) The hypobromite solution is prepared as follows. Add 20 g. of bromine slowly with vigorous shaking to 500 ml. of water containing 12 g. of sodium hydroxide. Dilute to 2 liters with water and store in a dark cupboard. This solution is approximately $0.12N$.

(2) Borax may be used in place of potassium bicarbonate and is perhaps to be preferred since there is no effervescence when the solution is acidified.

Kolthoff and Stenger[7] determined ammonia in ammonium salts by oxidizing with calcium hypochlorite in the presence of bromide in a bicarbonate medium. This procedure is free from the several sources of error which have been reported in the literature (p. 574).

Procedure: To 25 ml. of the solution of the ammonium salt (5–25 mg. of ammonia) add 1 g. of potassium bromide and 0.5 g. of sodium bicarbonate. Swirl the contents of the flask to promote dissolution of the solids and titrate with $0.1N$ calcium or sodium hypochlorite until a permanent light-yellow color (which indicates a slight excess of hypochlorite) appears. Set aside for 5 minutes and then add from a pipette 10 ml. of $0.01N$ sodium arsenite solution (obtained by appropriate dilution of the $0.1N$ solution). Add 1 drop of bordeaux indicator which should impart a pinkish color to the solution; if it fades there is insufficient sodium arsenite present. Continue the titration as in the titration of arsenite (p. 580).

Calculate the amount of hypochlorite equivalent to 10 ml. of $0.01N$ sodium arsenite solution, and deduct this value from the total amount of $0.1N$ hypochlorite solution consumed in the titration. The difference is equivalent to the amount of ammonia in the original solution.

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[36] Cf. J. Thiele, *Liebigs Ann.*, 273, 160 (1892).

Notes: (1) Tartrazine indicator may be used in place of bordeaux. Proceed as described on p. 581. The iodometric method may also be used and is to be preferred for very small amounts because the end-point is more sensitive.

(2) When copper or iron(III) is present, disodium hydrogen phosphate is to be preferred to sodium bicarbonate, for their colors then give less masking of the end-point. More than 10 mg. of potassium dichromate makes the indicator change less distinct.

(3) This titration has been applied to the determination of nitrogen in organic compounds.[37] Belcher and Bhatty carried out the digestion and titration of micro and semimicro samples in the same container.

It has also been applied to 50 μg. samples after sealed tube digestion[38]; in this case the iodometric method is to be preferred owing to its greater sensitivity.

(4) Slowick and Kelley[39] determined methenamine by decomposing with dilute sulfuric acid to give ammonium sulfate and then titrating ammonia as above.

Procedure: Dissolve 1 g. of sample in water and dilute to 200 ml. in a graduated flask. To a 10 ml. aliquot add 10 ml. of water, and 10 ml. of 10 per cent (w/v) sulfuric acid, and boil vigorously while adding more water at intervals until no smell of formaldehyde can be detected. Cool, add 1 drop of methyl red, neutralize with potassium bicarbonate, and add 3 g. of potassium bromide. Slowly add an excess of standard calcium hypochlorite, stopper the vessel, set aside for 5 minutes, and shake occasionally. Add 3 g. of potassium iodide dissolved in 15 ml. of 36 per cent acetic acid and titrate with 0.1N thiosulfate solution. Carry out a blank determination.

(5) Magnesium in the ash obtained from milk and blood was determined indirectly by Moto.[40] He precipitated as magnesium ammonium phosphate and then applied the sodium hypobromite procedure for the determination of ammonia.

Levy (p. 566) claimed that when the oxidation is done with bromine in a bicarbonate medium, the effects noted by Kolthoff and Laur are overcome. Several sources of error were indicated by Tschepelewetzky and Posdniakowa,[41] who stated that the optimum pH for oxidation was 7.5–9.5. In strongly alkaline solutions low results may be obtained because of some formation of nitrogen oxides which interfere in the iodometric back-titration; some ammonia may be volatilized and the reaction is said to be incomplete because of the high stability of ammonium hypobromite under these conditions. These observations should be considered in conjunction with those of Tomíček and Jasek (p. 574). Recently Köszegi and Salgó[42] have attributed the deviations from the theoretical, which Kolthoff and Laur noted, to a loss of bromine and to the presence of bromate in the hypobromite solution. They claim that these errors are prevented by the use of a special flask and by preparation of the hypobromite *in situ;* theoretical results are then obtained. If loss of bromine is indeed a cause of low results, it remains to be explained why the determination with a solution of hypochlorite in the presence of bromide gives excellent results.

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[37] P. Artmann and A. Skrabal, *Z. anal. Chem.*, **46**, 5 (1907); H. H. Willard and W. E. Cake, *J. Am. Chem. Soc.*, **42**, 2646 (1920); B. Levy, *Z. anal. Chem.*, **84**, 98 (1931); H. W. Harvey, *Analyst*, **76**, 657 (1951); R. Belcher and M. K. Bhatty, *Mikrochim. Acta*, **1956**, 1183.

[38] R. Belcher, T. S. West, and M. Williams, unpublished studies.

[39] E. F. Slowick and R. S. Kelley, *J. Am. Pharm. Assoc.*, **31**, 15 (1942).

[40] S. Moto, *Nisshin Igaku*, **39**, 155 (1952).

[41] M. Tschepelewetzky and S. Posdniakowa, *Z. anal. Chem.*, **84**, 106 (1931).

[42] D. Köszegi and E. Salgó, *Z. anal. Chem.*, **143**, 423 (1954); *Acta. Chim. Acad. Sci. Hung.*, **7**, 333 (1955).

Köszegi and Salgó[42] produce hypobromite *in situ* from a standard solution of bromate. They carry out the determination in a Schulek bromination flask (p. 29).

Procedure: Mix 40 ml. of 0.1*N* potassium bromate solution and 1.5 g. of potassium bromide in the flask and place the funnel in position. Evacuate the flask. Add 10 ml. of 2*N* hydrochloric acid through the funnel, taking care that a slight vacuum remains in the flask. Carefully run in 16 ml. of 2*N* sodium hydroxide, close the stopper, and shake to convert the bromine to hypobromite. Add the ammonia solution (which should be equivalent to about 20 ml. of 0.1*N* bromate). Close the flask and set aside for 20 minutes. Rinse the ground-glass joint. Add 1.5 g. of potassium iodide, 20 ml. of 2*N* hydrochloric acid and, after 5 minutes, 0.5 g. of sodium bicarbonate. Titrate with 0.1*N* thiosulfate using starch as indicator.

One milliliter of 0.1*N* bromate corresponds to 0.5677 mg. of ammonia.

Hydrazine: Bray and Cuy[43] determined hydrazine by adding excess of sodium hypochlorite to a buffered solution (pH = 7) of hydrazine sulfate. There is no loss of chlorine under these conditions and the reaction is rapid.

$$N_2H_4 + 2NaClO \longrightarrow N_2 + 2H_2O + 2NaCl$$

Procedure: To 50 ml. of the buffer solution (equimolecular mixture of mono- and disodium phosphate) add the solution of hydrazine sulfate, followed by an excess of standard hypochlorite solution. Set aside for 5 minutes, add potassium iodide, and acidify with sulfuric acid. Titrate the liberated iodine with a standard solution of thiosulfate.

Notes: (1) Tomíček *et al.*[8] state that low results are obtained unless potassium bromide is present.

(2) Erdey and Buzás[19] add 100 ml. of a buffer solution (60 ml. of 0.066*M* disodium hydrogen phosphate and 40 ml. of 0.066*M* potassium dihydrogen phosphate) and titrate directly at 80°C. with luminol as indicator (p. 577). Potassium bromide is not added, but presumably at the higher temperature the reaction goes rapidly to completion.

(3) Rupp and Mäder[44] determined hydroxylamine by oxidation with neutral hypobromite, but the conditions appear to be very critical. The original paper should be consulted for details.

$$2NH_2OH + NaClO \longrightarrow N_2 + 3H_2O + NaCl$$

It is to be noted that Riley *et al.*,[45] in a study of the reactions of hypobromite and hypochlorite with ammonia, hydrazine, and hydroxylamine, found that appreciable amounts of nitrogen oxides were formed with hydroxylamine; the other compounds formed only very small amounts. These investigators used N^{15} as a tracer in their experiments.

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[43] W. C. Bray and E. J. Cuy, *J. Am. Chem. Soc.*, **46**, 858 (1924).

[44] E. Rupp and H. Mäder, *Arch. Pharm.*, **251**, 295 (1913).

[45] R. F. Riley, E. Richter, M. Rotheman, N. Todd, L. S. Myers, and R. Nusbaum, *J. Am. Chem. Soc.*, **76**, 3301 (1954); cf. K. Clusius and G. Rechnitz, *Helv. Chim. Acta*, **36**, 59 (1953).

Hydrogen Peroxide: Hydrogen peroxide reacts quantitatively with hypochlorite.

$$OCl^- + H_2O_2 \longrightarrow Cl^- + H_2O + O_2$$

Bitskei[46] adds standard hypochlorite and determines the excess with standard arsenite. A solution of brasilin is used as indicator in the presence of potassium iodide as "catalyst."

Iodide: Willard and Fenwick[47] determined iodide by oxidizing with an excess of hypobromite and titrating with a standard solution of sodium arsenite to a potentiometric end-point.

$$I^- + 3BrO^- \longrightarrow IO_3^- + 3Br^-$$

Tomíček *et al.*[8] found that this method gives results about 1 per cent high. Schwicker, however, states that iodide may be determined in the presence of bromide by titrating with sodium hypochlorite.[48] The iodide is oxidized first to iodine and then to iodate; the end-point is taken when the blue starch-iodine color disappears. In the absence of bromides "after-blueing" occurs; hence it is necessary, in such cases, to add a few drops of 1 per cent potassium bromide solution.

$$I^- + 3ClO^- \longrightarrow IO_3^- + 3Cl^-$$

Procedure: To 20 ml. of the iodide solution (approximately $0.02M$) add 0.5–1 g. of sodium bicarbonate, dissolve, and titrate with $0.1N$ sodium hypochlorite solution until the solution is pale yellow. Add starch indicator and continue the titration until the starch-iodine color disappears.

Notes: (1) The sodium hypochlorite solution is prepared by treating 10 g. of calcium hypochlorite dissolved in water with a slight excess of 5 per cent sodium carbonate solution, and filtering. After assaying by the Pontius method (p. 263), it is diluted to $0.1N$.

(2) Saturated borax solution (5–10 ml.) may be substituted for the sodium bicarbonate.

(3) One milligram of iodide in the presence of 100 mg. of potassium bromide may be determined satisfactorily.

(4) Iodate and bromate in admixture may be determined as follows. Determine the total halate iodometrically. Reduce a further aliquot with 1 per cent potassium bisulfite in a sulfuric acid medium, and boil off the excess of sulfur dioxide; then determine iodide as above. Alternatively, reduce by titrating with bisulfite to the disappearance of the starch-iodine color, then proceed as above.

(5) Iodate, bromate, and iodide in admixture may also be determined by a combination of the above methods.

[46] J. Bitskei, *Acta. Chim. Acad. Sci. Hung.*, 8, 203 (1955); cf. F. Schonbein, *J. prakt. Chem.*, 77, 269 (1859).

[47] H. H. Willard and F. Fenwick, *J. Am. Chem. Soc.*, 45, 631 (1923).

[48] A. Schwicker, *Z. anal. Chem.*, 110, 173 (1937).

Bromide: Instead of transforming bromide to bromate with hypochlorite (p. 254), Farkas and Lewin[49] found conditions under which the reaction

$$ClO^- + Br^- \longrightarrow BrO^- + Cl^- \qquad (1)$$

goes quantitatively. The rate of the reaction decreases with increasing pH; in the pH range 9 to 10 the reaction is complete in a few minutes, whereas in the range 12 to 14 several hours are required. At lower pH other reactions involving the formation of chlorate and bromate take place simultaneously. Under the conditions given below, only reaction (1) occurs. The hypobromite which is formed is removed in strongly alkaline medium by reaction with phenol. Under these conditions, the excess hypochlorite does not react appreciably with phenol in 30 seconds and is determined with arsenic trioxide.

Procedure: Place the sample containing 40–80 mg. of potassium bromide in a 250 ml. Erlenmeyer flask. Add 15 ml. of standard 0.1*N* sodium hypochlorite and 1.7–2.0 ml. of 5 per cent boric acid solution as buffer; dilute, if necessary, to 25 ml. with water. After 5 minutes, add rapidly with vigorous shaking 6 ml. of 2*N* sodium hydroxide and 8 ml. of 0.5 per cent phenol. (If the initial volume of sample is larger than 8–10 ml., add more alkali to bring the final alkalinity to at least 0.25*N*.) Shake for 7 to 10 seconds, then quickly add 25 ml. of 0.1*N* sodium arsenite from a 50 ml. beaker. Rinse the beaker twice with distilled water and then 5 minutes later with 75 ml. of 5 per cent sodium bicarbonate solution. Add 2*N* acetic acid dropwise with vigorous shaking until carbon dioxide is evolved. Titrate the solution with 0.05*N* iodine solution to a permanent light blue with starch indicator. The temperature during the iodine titration should not exceed 20°C.

Notes: (1) Prepare the standard sodium hypochlorite solution by bubbling 70 g. of chlorine slowly through 1 liter of 9 per cent sodium hydroxide solution at 0–2°C. Dilute the solution to give approximately 0.1*N* hypochlorite solution with pH of 12.15. Keep the solution in a dark bottle in a refrigerator and standardize daily.

(2) When the sample contains less than 40 mg. of bromide, accurate analyses may be made using 0.04*N* hypochlorite, 0.04*N* arsenite, and 0.02*N* iodine solution. Proportionally smaller amounts of phenol should be used but the other conditions remain unchanged.

(3) The method is claimed to be accurate to 0.2 per cent.

(4) Alkaline earth metal salts up to a molar ratio to bromide of 10 do not interfere. At higher ratios, considerable errors are encountered because alkaline earth hydroxides tend to adsorb hypobromite, preventing its complete reaction with phenol. Up to 40 g. of sodium chloride per liter can be tolerated.

(5) For the determination of very small amounts of bromide, it is evident that the oxidation method to bromate (see p. 254) has several advantages.

Sulfide: Several methods have been described for the determination of sulfide which are based on oxidation with hypochlorite or hypobromite. Under ideal conditions the reaction proceeds

$$S^{2-} + 4OCl^- \longrightarrow SO_4^{2-} + 4Cl^-$$

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[49] L. Farkas and M. Lewin, *Anal. Chem.* 19, 665 (1947). cf. *idem, ibid.*, 662.

hence a very favorable titer is obtained. Unfortunately there is some disagreement about the stoichiometry of the reaction and few investigators appear to be capable of confirming each other's results. It must be admitted that there is still room for extensive investigation on this reaction in order to clear up the doubtful points and conflicting claims.

According to Choppin and Faulkenberry,[50] when sulfide is oxidized with hypochlorite, the end-products of the reaction are sulfur and sulfate in amounts which depend on the concentration of the reactants, the temperature, and the hydrogen-ion concentration. When the reactants are of approximately the same concentration, the relative amounts of sulfur and sulfide produced are constant for dilute solutions. The formation of sulfur increases with sulfide concentration, and that of sulfate with hypochlorite concentration. Increase of temperature favors the formation of sulfate because the oxidation rate of colloidal sulfur is increased. There is a distinct minimum in the formation of sulfate at about pH 10.

Tomíček *et al.*[8] reported difficulties when sulfide was oxidized with sodium hypobromite or with calcium hypochlorite in the presence of bromide owing to the formation of colloidal sulfur. Their tests were done under various conditions. Pepkowitz[51] determined small amounts of sulfide by an evolution method in which the evolved hydrogen sulfide was absorbed in an excess of calcium hypochlorite standardized empirically against a sodium sulfide solution which had been evaluated against a standard iodine solution. Dunicz and Rosenqvist[52] stated that the extent of oxidation under Pepkowitz's conditions was nearer 50 than 100 per cent. Oxidation is approximately quantitative at pH 8–11 and pH 14–15; it is at a minimum at pH 12 (cf. Choppin and Faulkenberry[50]). Since commercial calcium hypochlorite has a pH of approximately 12, this may account for the irregular results obtained with this reagent. Accordingly, they recommended the use of potassium hypochlorite (prepared by passing pure chlorine gas into a solution of potassium hydroxide). Since it is more convenient to work at the higher optimum pH range, sufficient potassium hydroxide (3.5 g. per 25 ml. of potassium hypochlorite) is added to give a pH of 14.4. Kitchener, Lieberman, and Spratt[53] absorbed hydrogen sulfide directly into sodium hypochlorite solution when determining sulfur in steels. They noted that some colloidal sulfur is formed but they convert this to sulfate by boiling the hypochlorite solution. It is stated that during the first 2 minutes of boiling there is a slight loss of titer, amounting to 0.7 per cent; thereafter the titer remains constant. This initial loss is ascribed to the presence of traces of organic matter.

Bethge[54] examined iodine, sodium hypochlorite, potassium permanganate, and potassium iodate as oxidants for sulfide. He concluded that the best results are obtained with an alkaline solution of standard potassium iodate.[55]

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[50] A. R. Choppin and L. C. Faulkenberry, *J. Am. Chem. Soc.*, 59, 2203 (1937).

[51] L. P. Pepkowitz, *Anal. Chem.*, 20, 968 (1948).

[52] B. L. Dunicz and T. Rosenqvist, *Anal. Chem.*, 24, 404 (1952).

[53] J. A. Kitchener, A. Lieberman, and D. A. Spratt, *Analyst*, **76**, 509 (1951).

[54] P. O. Bethge, *Anal. Chim. Acta*, 9, 129 (1953); 10, 113, 310 (1954).

[55] This is confirmed by S. Ignatowicz, British Iron and Steel Assoc., private communication.

The yield is never 100 per cent when the hypochlorite method is used; it improves with increase in alkalinity and temperature, but, at 100°C. and in a concentration of $5N$ in hydroxide, the yield is only 96 per cent owing to decomposition of the hypochlorite. (See Table II.) Direct titrations with hypochlorite and hypobromite have been reported by Erdey and Buzás[19] and by Bitskei and Forhencz.[14]

TABLE II

Oxidation of Sodium Sulfide with Sodium Hypochlorite under Various Conditions

Normality of alkali	Completeness of oxidation compared with iodine method (per cent) 20°C.	100°C.
0.4	69	95
1.0	82.6	97.6
2.5	98.1	98.3
5.0	99.1	96

The importance of maintaining a high concentration of alkali was first pointed out by Willard and Cake.[56] They observed that oxidation is complete with hypobromite at an alkali concentration greater than $2.5N$; and with hypochlorite at an alkali concentration greater than $4N$. The method they described is given below.

Procedure: Add sufficient standard sodium hypobromite or hypochlorite to the alkaline solution of sulfide so that not more than two thirds is consumed in the reaction. Set aside for 3–5 minutes, add 2–3 g. of potassium iodide, dilute to 4–5 times the original volume, neutralize with concentrated hydrochloric acid (until the iodine color appears), and add 3–5 ml. in excess. Titrate with standard thiosulfate solution.

Notes: (1) *Sodium Hypobromite Solution:* Add 100 g. of bromine while cooling to 60 g. of sodium hydroxide dissolved in 1600 ml. of water. Standardize iodometrically and store in the dark. Since traces of metals increase the rate of decomposition it is advisable to allow the alkali solution to stand for several days before the bromine is added and then to filter or siphon from the residue.

Sodium Hypochlorite Solution: Pass dry chlorine gas into a solution consisting of 90 g. of sodium hydroxide dissolved in 1500 ml. of water until the weight is increased by 35 g. The solution is more stable than that of hypobromite.

(2) The titration was applied to the determination of sulfur in steels by the evolution method and to precipitated metal sulfides. It is not applicable to natural sulfides.

(3) Leitch[57] determined some organic sulfides by direct titration with sodium hypochlorite in a slightly acid medium. He used methyl orange as irreversible indicator. It is not possible to assess the general accuracy of the method, for the determinations were done on aqueous solutions and the results expressed as a "chlorine factor."

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[56] H. H. Willard and W. E. Cake, *J. Am. Chem. Soc.*, **43**, 1610 (1921).

[57] J. L. Leitch, *J. Franklin Inst.*, **239**, 334 (1945).

Sulfite: Sulfite is oxidized to sulfate by hypobromite:

$$SO_3^{2-} + BrO^- \longrightarrow SO_4^{2-} + Br^-$$

Bonner and Yost[58] stated that sulfite can be determined in alkaline solution by adding an excess of 0.1*N* sodium hypochlorite, diluting to 150 ml. and then determining the unconsumed hypochlorite iodometrically. Tomíček *et al.*[8] were unable to obtain satisfactory results by direct titration with either hypobromite or hypochlorite. They suggest that better results might be obtained by titrating the sulfite directly into hypochlorite.

Erdey and Buzás[19] have reported a direct titration with sodium hypobromite. The solution of sulfite contains 2–10 ml. of *N* sodium hydroxide, and luminol is used as indicator (p. 577).

Thiosulfate: Hypobromite oxidizes thiosulfate as follows.[59]

$$S_2O_3^{2-} + 4BrO^- + H_2O \longrightarrow 2SO_4^{2-} + 4Br^- + 2H^+$$

In the direct titration with sodium hypobromite high results are obtained,[8] but with calcium hypochlorite in the presence of bromide the results are exact; in the absence of bromide the results are low. Overholser[60] recommends adding an excess of reagent and determination of the excess.

Procedure: To 25 ml. of the solution of thiosulfate add 1 g. of potassium bromide and 1 g. of sodium bicarbonate. Add an excess of 0.1*N* calcium hypochlorite solution, then 10 ml. of 0.01*N* sodium arsenite (p. 43), and titrate with the hypochlorite solution in the presence of bordeaux as indicator. Correct the titer for the amount of sodium arsenite added and make the usual indicator corrections.

Notes: (1) Borax may be used in place of sodium bicarbonate.

(2) The iodometric method may also be used (p. 580). Direct titration methods have also been described.[14,19]

Thiocyanate: Thiocyanate is oxidized by hypobromite according to the reaction:

$$CNS^- + 4BrO^- + H_2O \longrightarrow CNO^- + 4Br^- + 2H^+ + SO_4^{2-}$$

Tomíček and Jašek[8,61] obtained results about 2–4 per cent too high in their potentiometric studies in which direct titration with a solution of sodium hypobromite was used. In later experiments, however, when calcium hypochlorite was used good results were obtained. The reason for these differences has already been discussed (p. 574). From experiments carried out by Overholser[60] it appears that a direct titration with bordeaux as indicator is satisfactory.

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[58] W. D. Bonner and D. M. Yost, *Ind. Eng. Chem.*, **18**, 55 (1926).

[59] Cf. V. A. Willson, *Ind. Eng. Chem., Anal. Ed.*, **7**, 44 (1935).

[60] L. Overholser, unpublished studies.

[61] Cf. H. Rechmann, *Z. anal. Chem.*, **130**, 39 (1949).

Procedure: To 25 ml. of the solution of thiocyanate add 1 g. of potassium bromide and 1 g. of sodium bicarbonate. Titrate slowly with 0.1*N* calcium hypochlorite until the end-point is approached and then add 1 drop of bordeaux indicator. Complete the titration in the usual way (p. 580) and deduct the indicator blank. A precipitate of calcium carbonate forms during the titration but does not disturb the titration in any way.

Cyanide: Cyanide is oxidized by hypobromite or hypochlorite according to the reaction:

$$CN^- + BrO^- \longrightarrow CNO^- + Br^-$$

When cyanide is titrated in the presence of bicarbonate, Tomíček and Filipovič[3] noted that a spontaneous atmospheric oxidation occurred during the titration. They recommended that a preliminary titration should be done and then almost the whole of the amount of titrant should be added to a second sample and the titration completed dropwise. In these titrations good results were obtained with calcium hypochlorite with or without the addition of potassium bromide.

Overholser[60] determines cyanide in exactly the same way as thiocyanate, but makes no reference to the phenomenon noted above.

Notes: (1) Golse[62] determines cyanide in mercuric cyanide by adding it to an excess of hypobromite and then following with an iodometric titration. The reaction is probably as follows:

$$Hg(CN)_2 + 2NaBrO + 2NaBr \longrightarrow Na_2HgBr_4 + 2NaCNO$$

(2) Cochineal[14] and luminol[19] have been used as indicators in direct titration of cyanide.

Nitrite: In the direct titration of hypochlorite with standard nitrite solution, the end-point can be detected by means of iodine-starch paper.[63] Nitrite can be titrated directly both potentiometrically and amperometrically with hypochlorite but the reaction is slow.[64] There is no suitable indicator for the direct visual titration; reasonably accurate results can be obtained by adding an excess of hypochlorite to the nitrite solution which contains bicarbonate, allowing the solution to stand for 15 minutes and completing the titration in the usual way after having added an excess of sodium arsenite. Bordeaux, tartrazine, or quinoline yellow (p. 578) may be used as indicator. The accuracy is within 1 per cent for 0.1*N* nitrite and 2 per cent for 0.01*N* nitrite solutions.

Phosphite: Manchot and Steinhäuser[65] found that their bromometric titration (p. 564) could be applied to the determination of phosphite if a bicarbonate or acetate medium was used. Kolthoff[66] modified the procedure by using a hypobromite solution.

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[62] J. Golse, *Bull. soc. chim. France*, (4) 45, 177 (1929).

[63] Z. Kertész, *Z. angew. Chem.*, 36, 595 (1923); 37, 23 (1924); *Z. anal. Chem.*, 74, 105 (1928); cf. H. Kauffmann, *Leipzig. Monatschr. Textil-Ind.*, 1927, 40, 111.

[64] Chi Chang, unpublished work, University of Minnesota.

[65] W. Manchot and F. Steinhäuser, *Z. anorg. u. allgem. Chem.*, **138**, 304 (1924).

Procedure: To 10 ml. of approximately $0.05M$ phosphite solution in a glass-stoppered flask, add 25 ml. of $0.1N$ hypobromite solution and 1–2 g. of sodium bicarbonate. Stopper the flask and set aside for 30–60 minutes. Titrate the excess of hypobromite iodometrically.

Schwicker[67] determined phosphorous acid by oxidizing to phosphate with an excess of sodium hypochlorite. Calcium hypochlorite is unsuitable for this determination, for insoluble calcium phosphite is produced and the oxidation is then incomplete. The solution of sodium hypochlorite is prepared by adding sodium carbonate to a calcium hypochlorite solution and filtering off the precipitate; it is standardized by the Pontius method (p. 263). Hypophosphites do not interfere.

Procedure: Neutralize 10–20 ml. of approximately $0.05M$ phosphorous acid with sodium bicarbonate, add an excess of standard sodium hypochlorite solution, and set aside for 10 minutes. Add 1 g. of sodium bicarbonate and starch indicator and titrate with $0.015N$ potassium iodide to the first appearance of a blue color (cf. p. 263).

Selenite: Van der Meulen[68] has described the following method for the determination of selenites.

$$\mathrm{SeO_3^{2-} + BrO^- \longrightarrow SeO_4^{2-} + Br^-}$$

Procedure: To 40 ml. of an approximately $0.05M$ solution of the selenite add 10 ml. of N potassium bicarbonate solution and 25 ml. of $0.2N$ hypobromite solution (16 g. of bromine in 500 ml. of water mixed with 12 g. of sodium hydroxide dissolved in 100 ml. of water and diluted to 1 liter). Dilute with 50 ml. of water and add 10 ml. of N potassium iodide solution, 5 ml. of $5N$ hydrochloric acid, and a few drops of molybdate catalyst (p. 256). Titrate the iodine with $0.1N$ thiosulfate.

One milliliter of $0.1N$ hypobromite corresponds to 3.96 mg. of selenium.

Note: Methods have also been described for elementary selenium and mixtures.[68] Willard and Manalo[18] were unable to obtain satisfactory results for direct titration, but Tomíček and Filipovič[8] titrated potentiometrically and found that oxidation was rapid and quantitative with either hypobromite or hypochlorite solution.

3. Determination of Organic Compounds. *Urea:* It has already been stated (p. 573) that urea may be determined by oxidation with hypochlorite or hypobromite; in the early methods the volume of nitrogen produced was measured:[69]

$$\mathrm{(NH_2)_2CO + 3BrO^- \longrightarrow CO_2 + N_2 + 2H_2O + 3Br^-}$$

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[66] I. M. Kolthoff, *Pharm. Weekblad,* **53,** 913 (1916).

[67] A. Schwicker, *Z. anal. Chem.,* **110,** 161 (1937).

[68] J. H. van der Meulen, *Chem. Weekblad,* **31,** 333 (1934).

[69] Cf. H. J. H. Fenton, *J. Chem. Soc.,* **33,** 300 (1878); **35,** 12 (1879); W. Foster, *ibid.,* **33,** 470 (1878).

Some of the sources of error in the hypobromite method have been discussed by Margosches and Rose.[70] A more detailed study of the titrimetic method was made by Wölfel,[71] who considered that the main source of error was due to the formation of cyanate. This could be overcome by adding mineral acid to convert cyanate to ammonium salts[72] and then adding more alkaline hypobromite. He concluded that the method is satisfactory (±0.5 per cent) when certain precautions are taken:

1. The addition of potassium iodide before the final acidification.

2. The use of hypobromite solution at least $0.5N$ in concentration because the incompleteness of reaction increases with decrease in concentration.

3. The addition of sodium phosphate after the final acidification to overcome "after-blueing" effects caused by the formation of nitrite and the presence of bromate in the hypobromite. [Addition of urea to remove nitrogen oxides would undoubtedly be simpler. Authors.]

4. By standardizing the hypobromite solution empirically against urea following the procedure exactly. Wölfel also noted that varying the composition of the hypobromite solution did not diminish the formation of cyanate.

Tomíček and Filipovič,[8] in their potentiometric studies of the oxidizing properties of calcium hypochlorite in the presence of bromide (p. 574), found that oxidation was negligible at room temperature and that it was necessary to heat the solution containing urea to 90–95° C. Some transitory formation of hydrazine occurred. Even under these conditions the results were 5–6 per cent low and, in agreement with the findings of Wölfel, this was shown to be due to the formation of cyanate. Accordingly, after the potentiometric end-point had been reached, the hot solution was acidified with sulfuric acid and, after being cooled, was treated with sodium bicarbonate and an excess of hypochlorite; it was back-titrated with a standard arsenite solution. Even under these conditions, the most favorable found, the error was −1.3 to −2.8 per cent.

Possibly the method of Artmann and Skrabal, as modified by Kolthoff and Laur for the determination of ammonia (p. 583) would give satisfactory results if the above precautions of Wölfel were taken into consideration. Likewise, the hypochlorite method of Kolthoff and Stenger for ammonia in which visual titration is used (p. 583) might also be applicable provided that the necessary precautions are taken.

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[70] B. M. Margosches and H. Rose, *Biochem. Z.*, **137**, 542 (1923); a complete bibliography of the older methods is given in this paper.

[71] K. Wölfel, *Z. anal. Chem.*, **90**, 170 (1932).

[72] Cf. E. A. Werner, *J. Chem. Soc.*, 121, 2318 (1922).

Procedure:[71] Transfer 50 ml. of the neutral solution containing 0.02–0.2 g. of urea to a 600 ml. flask fitted with a ground stopper which carries a delivery funnel and a Göckel-Contat trap. Add sufficient $0.5N$ hypobromite solution to give an excess of one third to one half of the theoretical amount. (Not less than 15 ml. should be added.) After 5 minutes dissolve 3–5 g. of potassium bromide in the solution. Charge the trap with a solution containing 3–4 g. of potassium iodide (for blank determinations 8–10 g.). Introduce 15 ml. of $5N$ hydrochloric acid into the flask through the delivery funnel and after 5 minutes add 15 ml. of $5N$ sodium hydroxide in the same way. After several minutes most of the iodide solution is drawn into the flask from the trap. Then add 15 ml. of $5N$ hydrochloric acid while cooling the flask in water. Shake until all iodine vapor has redissolved in the solution. After 5 minutes transfer the remainder of the iodide solution quantitatively to the flask and dissolve 10–12 g. of disodium hydrogen phosphate dodecahydrate in the solution, which should by now have reached a volume of 200 ml. Titrate the excess of hypobromite with $0.5N$ thiosulfate solution.

Standardize the hypobromite solution in exactly the same way against standard thiosulfate, but omit the addition of sodium hydrogen phosphate.

Benzenesulfinic Acid: Ackerman[73] investigated Thomas's reaction[74] of sodium benzenesulfinate with hypochlorite and found conditions under which the reaction is quantitative.

$$C_6H_5SO_2Na + NaOCl \longrightarrow C_6H_5SO_3Na + NaCl$$

A small amount of sulfinyl chloride may be formed but this has no effect on the titration because the consumption of hypochlorite is not affected by the reaction:

$$C_6H_5SO_2Na + NaOCl + H_2O \longrightarrow C_6H_5SO_2Cl + 2NaOH$$

Procedure: Transfer the sample S (about 2.5 g.) of sodium benzenesulfinate to a 250 ml. flask, dilute to about 150 ml., and make slightly alkaline with sodium hydroxide (brilliant yellow indicator paper). In order to remove sulfite and sulfate which may be present in commercial samples, add 10 ml. of 10 per cent barium chloride and digest the precipitate for 30 minutes on a water bath. Filter, wash into a 250 ml. graduated flask, and dilute to the mark (solution A).

Dilute 20 ml. of 12 per cent sodium hypochlorite to 1 liter (solution B). Titrate 50 ml. of this solution with $0.1N$ sodium arsenite until the indicator paper (Note) no longer gives a blue color when spotted with a drop of test solution (titer $= b$).

Transfer 50 ml. of solution B to a flask, add 50 ml. of 10 per cent sodium carbonate solution and 100 ml. of water, and cool to 15°C. Titrate this with solution A until the test paper no longer gives a blue color when spotted with a drop of solution B (titer $= s$).

$$\frac{b \times 0.016416 \times 100}{2 \times (s/250) \times S} = \frac{205.2 \times b}{s \times S} = \text{per cent sodium benzene sulfinate}$$

Note: The starch-iodine test paper must be very sensitive and is prepared as follows.

Boil 1 liter of water for several minutes, add 3 g. of pure cadmium iodide crystals and 5 g. of potato starch made into a thin paste with water. Boil for several minutes and allow to settle for several hours. Decant the clear liquor. Pass strips (12.5 cm. wide) of Reeves-Angel filter paper No. 211 through the solution and dry in a dust- and fume-free atmosphere. Use strips 1.25 x 12.5 cm.

[73] L. Ackerman, *Ind. Eng. Chem., Anal. Ed.*, 18, 243 (1946).

[74] J Thomas, *J. Chem. Soc.*, **95**, 342 (1909).

Other Organic Compounds: Tomíček *et al.*[8] attempted unsuccessfully to determine hydroquinones, phenol, thymol, aniline, sulfanilic acid, and 8-hydroxyquinoline. Glycerol was determined by Cuthill and Atkins[75] by boiling for 90–180 minutes with a slight excess of sodium hypobromite. The method does not appear to be very satisfactory. Friedman and Morgulis[76] determine amino acids by oxidation with hypobromite under various conditions. Exact details of the determinations are not given. The oxidation of amino acids by hypochlorite was also studied by Gordon.[77]

Aromatic sulfonic acid amides have been determined by thermometric titration with sodium hypochlorite in alkaline solution.[78]

Cattelain[79] has determined 3-thioketo-5-keto-6-benzyl-1,2,4-triazine by titrating it with standard sodium hypobromite in the presence of phenolphthalein as indicator. The latter is bleached at the end-point.

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[75] R. Cuthill and C. Atkins, *J. Soc. Chem. Ind.*, 57, 89 (1938).

[76] A. H. Friedman and S. Morgulis, *J. Am. Chem. Soc.*, 58, 909 (1936).

[77] H. T. Gordon, *Anal. Chem.*, 23, 1853 (1951).

[78] H. Shäfer and E. Wilde, *Z. anal. Chem.*, 130, 396 (1950).

[79] E. Cattelain, *Ann. Chim. anal.*, 24, 150 (1942).

CHAPTER XIV

TITRATIONS WITH IRON(II), TITANIUM(III), AND OTHER STRONG REDUCING AGENTS

There are several strong reducing agents in use to which occasional reference has been made in cases where they have been used in conjunction with a suitable oxidimetric agent. Many of these reagents are more often used for direct titrations, e.g., titanous and chromous chlorides or sulfates, hence it is necessary to consider their uses more fully in a special section. It is also convenient to include in this chapter other reducing agents which, although generally used in conjunction with an oxidimetric reagent, find occasional use as direct titrants, e.g., ferrous sulfate.

With certain of these titrants the end-points are almost always determined potentiometrically, and it is without the scope of this text to consider such processes in detail. Accordingly, the treatment of chromous salts (p. 630) in view of their obvious importance may appear to be somewhat cavalier, but the applications of this titrant where visual end-points are used are not of sufficient practical value to warrant detailed description.

The redox potentials of the titrants discussed in this chapter are given in Table I.

TABLE I

Titrant	Reduced form	Oxidized form	E_0 (in volts)
Chromous	Cr^{2+}	Cr^{3+}	−0.41
Vanadous	V^{2+}	V^{3+}	−0.2
Titanous	Ti^{3+}	TiO^{2+}	+0.1
Stannous	Sn^{2+}	Sn^{4+}	+0.15
Ascorbic acid	$C_6H_8O_6$	$C_6H_6O_6$	+0.18
Ferrous	Fe^{2+}	Fe^{3+}	+0.77
Mercurous[1]	Hg_2^{2+}	Hg^{2+}	+0.92

[1] Cf. p. 623.

Storage of Air-Sensitive Solutions: Most of the titrants which are considered in this chapter are very sensitive to atmospheric oxidation and must be stored under an inert gas. Especial care must be taken with chromous, titanous, vanadous, and stannous solutions. Many different types of storage apparatus have been described in the literature. A conventional type of tank is shown in Volume II, p. 14, but several other arrangements are worthy of note.

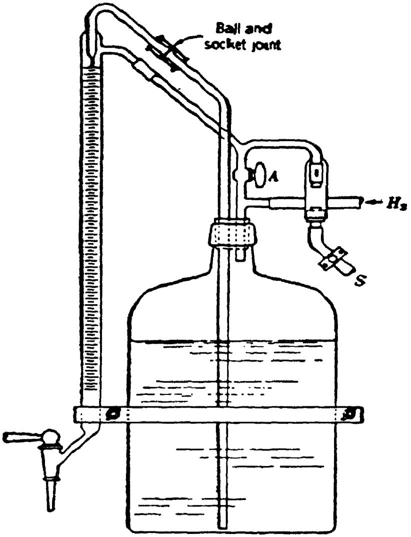

FIG. 1. Storage apparatus for titanous solutions.[2]

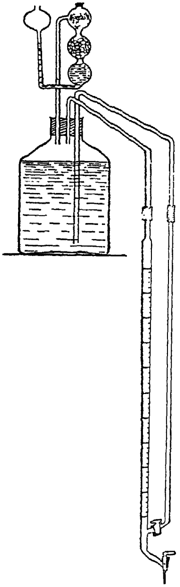

FIG. 2. Storage apparatus for stannous solutions.[3]

Smith and Getz[2] use the type shown in Fig. 1 for titanous solutions. To fil the burette, suction is applied at S with stopcock A closed; hydrogen is supplied from a suitable generator attached to H_2.

Szabó and Sugar[3] recommend the gravity-type apparatus shown in Fig. 2

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[2] G. F. Smith and C. A. Getz, *Ind. Eng. Chem., Anal. Ed.*, 6, 252 (1934); cf. E. Zintl and G. Rienäcker, *Z. anorg. Chem.*, 155, 84 (1926).

[3] Z. G. Szabó and E. Sugar, *Anal. Chim. Acta*, 6, 293 (1952).

for stannous solutions. This is one of the simplest types available but would probably be unsuitable for solutions which are more air-sensitive than those of stannous tin. The solution is prepared (p. 621) in the storage tank under carbon dioxide produced from marble chips in the acid solution. The small gas generator is then placed in position; the lowest bulb contains concentrated hydrochloric acid, the middle one marble chips, and the highest, glass wool. When liquid is withdrawn from the burette the acid rises into the marble, thus forming more carbon dioxide. The solution reaches equilibrium about 5 days after preparation and thereafter its titer decreases only very slowly.

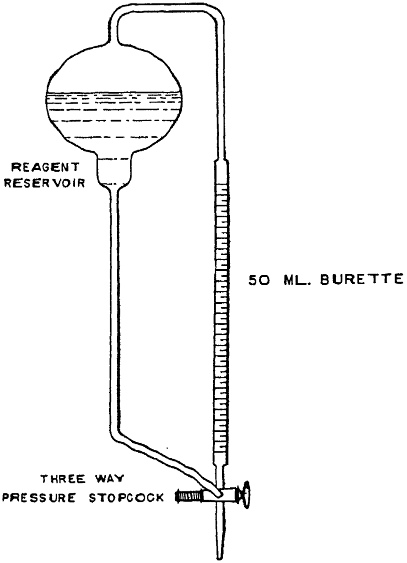

Fig. 3. Storage apparatus for chromous solutions.[4]

When very sensitive solutions, such as chromous or titanous, are used it is preferable to remove all traces of oxygen from the inert gas under which the solution is stored. Stone[4] found that carbon dioxide from commercial cylinders was satisfactory, but that nitrogen from a similar source required treatment. Nowadays tanks of pure nitrogen are available commercially. The best method is to pass the gas through a sintered-glass bubbler in a solution which is about 0.1N in chromous and 1N in sulfuric acid; a layer of amalgamated zinc at the bottom of the bottle serves to regenerate the chromous solution continuously.[5]

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[4] H. W. Stone, *Anal. Chem.*, 20, 747 (1948).

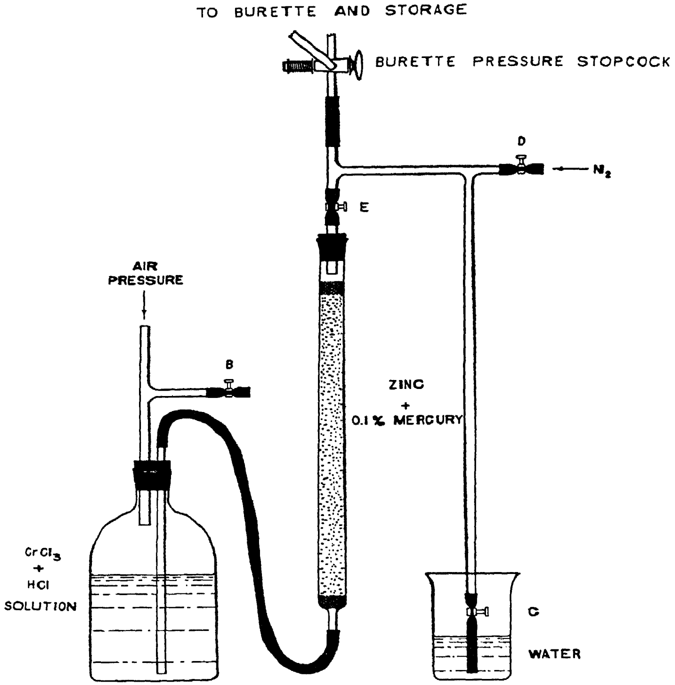

FIG. 4. Apparatus for preparation of chromous solutions.[4]

Stone[4] described a pressure-differential and a gravity-type apparatus for use with chromous solutions; the latter design (Fig. 3) is more generally useful. A 0.03N chromous solution prepared and stored as below retained its titer for 10 months; the method is therefore very serviceable when the titrant is required only occasionally. Chromous solutions are not dealt with in detail in this text (cf. p. 630), for their applications are mainly potentiometric. However, it seems worth while to describe Stone's procedure in detail since the principle could be adapted to the preparation of other solutions.

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[5] H. W. Stone and C. Beeson, *Ind. Eng. Chem., Anal. Ed.*, 8, 188 (1936).

Procedure: The stopcock at the top of Fig. 4 corresponds to that of the burette in Fig. 3. Close screw clip D and open those at B, C, and E. Pass in air at about 1 atmosphere above room pressure and close clip B gradually until the chromic solution rises through the zinc amalgam reductor and into C, thus clearing the line of air. Open the burette tap and close C so that the chromous solution rises into the reservoir; regulate the rate of flow by clip B. When enough solution is present in the burette and reservoir to absorb all oxygen, close clip E and the burette tap and shake to complete the removal of oxygen. To balance the resultant decrease in pressure, introduce nitrogen through D into the burette. The nitrogen pressure, regulated by a pressure-reducing valve on the gas cylinder, should be slightly greater than atmospheric pressure. Shake the apparatus, after closing the burette tap, to remove any oxygen introduced with the nitrogen. Close D and allow the partly spent chromous solution to flow into C. Adjust the system to about 1 atmosphere pressure of nitrogen by venting the gas through C. Fill the reservoir with chromous solution by closing C, opening E, and forcing the solution to rise by adjusting clip B.

Notes: (1) The reservoir should only be half-filled to avoid any danger from high pressure.

(2) Hydrogen can be used instead of nitrogen; carbon dioxide is unsatisfactory because the solubility varies too greatly with pressure and temperature and bubbles are formed in the burette tip.

In recent years, several types of apparatus containing metal reductors have been described which avoid the need for frequent restandardization of solutions and special precautions against atmospheric oxidation during storage. For ferrous solutions, Duke[6] inserted a 30 cm. "calcium chloride" tower between the storage tank and the burette; the upper part of the tower is filled with lead amalgam between two layers of glass wool. Thus any ferric iron in the solution is reduced before it passes into the burette; the lead does not reduce hydrogen ions, so that no gas is formed. The ferrous sulfate should be greater than 1*M* in sulfuric acid for rapid and quantitative reduction. Erdey *et al.*[7] used a cadmium or aluminum reductor attached to a large storage tank to obtain a ferric-free ferrous solution, but only applied the arrangement to avoid large blanks in methods where excess ferrous iron was added and the ferric iron formed was titrated with ascorbic acid (p. 627).

Flaschka[8] modified an ordinary burette by inserting a 20 cm. length of glass tubing above the stopcock and filling this with cadmium or silver powder; the solution must not be too acid and should flow through at about 3 drops per second. This "reductor burette" is suitable for titanous or ferrous solutions.

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[6] F. R. Duke, *Ind. Eng. Chem., Anal. Ed.*, **17**, 530 (1945); cf. P. Wehber and H. Hahn, *Z. anal. Chem.*, **136**, 321 (1952).

[7] L. Erdey, I. Buzás, and E. Bodor, *Acta Chim. Acad. Sci. Hung.*, **7**, 287 (1955).

[8] H. Flaschka, *Anal. Chim. Acta*, **4**, 242 (1950); *Mikrochemie*, **38**, 15 (1951).

FERROUS SALTS

The use of ferrous solutions for the determination of various oxidizing substances has been considered previously in other parts of the text. Although it is often preferable when determining ions such as permanganate, dichromate, and cerium(IV) to add an excess of ferrous solution and then to back-titrate with a standard oxidimetric reagent, sometimes it may be more convenient to carry out a direct titration with the ferrous solution; for example, chromium in steels is generally determined in this way. Only direct titrations will be considered in this section.

A slightly acid solution of ferrous iron (about 0.5–1*N* in sulfuric acid) is fairly stable and atmospheric oxidation is not very rapid. In neutral or strongly acidic solutions (with sulfuric or hydrochloric acid) the oxidation rate is considerably raised. In any case it is recommended that the ferrous solution be standardized before use on all occasions (e.g., against potassium dichromate with diphenylamine sulfonic acid as indicator, p. 177; in this case, ferroin would also be suitable, p. 173). Generally, ferrous ammonium sulfate, $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ (Mohr's salt) (p. 56) is to be preferred to ferrous sulfate for preparing the solution.

When it is important to ensure the complete absence of ferric salts, suitable storage apparatus may be employed. The reductor burettes described on p. 601 are useful for this purpose.

Manganese: Manganese(II) is not oxidized by chromic acid alone; however, if arsenious acid is also added the oxidation of Mn(II) is induced.

$$2Mn^{2+} + Cr_2O_7^{2-} + 2As^{3+} + 14H^+ \longrightarrow 2Mn^{3+} + 2Cr^{3+} + 2As^{5+} + 7H_2O$$

The reaction can only proceed quantitatively to the right if the trivalent manganese produced is complexed with hydrofluoric acid. On this basis, Lang and Kurtz[9] developed a new titration of manganese. The addition of hydrofluoric acid serves the purpose of preventing the reduction of the trivalent manganese by the excess of arsenious acid and of avoiding the oxidation of divalent manganese beyond the trivalent state.

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[9] R. Lang and F. Kurtz, *Z. anorg. Chem.*, 181, 111 (1929); cf. R. Lang and J. Zwerina, *ibid.*, 170, 387, 389 (1928).

From the above equation, $^1/_2$ millimole of dichromate is required for 1 millimole of manganese(II). However, the amount of arsenious acid added must not be based on this equation, because with decreasing amounts of manganous ion the ratio alters and when no manganese(II) is present the reaction proceeds as follows:

$$3As^{3+} + 2Cr^{6+} \longrightarrow 3A^{5+} + 2Cr^{3+}$$

For $^1/_2$ millimole of dichromate, at least $^3/_4$ millimole of arsenic trioxide should be present. The manganic complex formed is titrated with ferrous sulfate; diphenylamine or diphenylbenzidine serves as indicator. Under the given conditions, the color change from blue to green is very sharp. (According to Lang and Kurtz the indicator correction is only 0.01 ml. of 0.1*N* ferrous solution; cf. p. 175.) Diphenylaminesulfonic acid could undoubtedly also be used and would be preferable in the presence of tungstate.

Procedure (*a*): Add sodium hydroxide or sodium carbonate to the manganese solution containing less than 0.2 g. of manganese, to give a slightly alkaline mixture. If the test solution contains much iron, add alkali until there is an abundant and permanent precipitate. Add 5–10 ml. of hydrofluoric acid and 5–10 ml. of syrupy phosphoric acid followed by 45 ml. of approximately 0.3*N* potassium dichromate and 50 ml. of approximately 0.3*N* arsenic trioxide. Set aside for 2–3 minutes. Add 3 drops of 1 per cent diphenylamine solution and titrate with 0.1*N* ferrous sulfate in 0.2*N* sulfuric acid solution until the color changes from dark blue to grass green.

Procedure (*b*): To the neutral or slightly acidic manganese solution, add 25 ml. of 5*N* sulfuric acid and 5 g. of sodium fluoride and shake until the salt is dissolved. Add 5–10 ml. of syrupy phosphoric acid, 45 ml. of the dichromate solution, and continue as in method (*a*).

Notes: (1) Iron, cobalt, nickel, copper, tin, zinc, chloride, and nitrate do not interfere. Lead, which precipitates as sulfate, need not be removed. Tungstate also does not interfere when it is first dissolved in hydrofluoric acid or sodium fluoride. In this case, the phosphoric acid must always be added after the hydrofluoric acid; otherwise the indicator is unsatisfactory. Diphenylaminesulfonic acid indicator would not be affected by tungstate under any conditions. Mercuric salts interfere by bleaching the indicator at slight acidities. Large amounts of ammonium salts are detrimental.

(2) The procedure can also be applied to the determination of manganese in steels.[9]

The above method is unsatisfactory in the presence of aluminum, calcium, and magnesium because the fluorides precipitate and adsorb a small amount of manganous ion. Lang[10] found later that these cations did not interfere if metaphosphoric acid and sulfuric or nitric acid were substituted for hydrofluoric acid and orthophosphoric acid, respectively. In the induced oxidation, a manganic-metaphosphoric acid complex is then formed which is stable to strong sulfuric acid. The procedure gives accurate results.

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[10] R. Lang, *Z. anal. Chem.*, 102, 8 (1935).

Procedure: Dilute the chloride-free manganese solution which contains 5–40 ml. of concentrated sulfuric acid or 15–50 ml. of nitric acid (sp. gr. 1.42) (freed from nitrogen oxides with urea) to 180 ml. and cool to room temperature. Add sufficient metaphosphoric acid (see Note 2) dissolved in 20–25 ml. of water and 3 drops of 1 per cent diphenylamine indicator. Add, with shaking, dichromate solution (15 g. of potassium dichromate per liter) and then an excess of arsenite solution (15 g. of arsenic trioxide and 10 g. of sodium carbonate per liter). Titrate after 30 seconds with 0.1*N* ferrous sulfate in 1 per cent sulfuric acid. The color changes from deep red through violet to blue and finally to green. The pure blue color is obtained about 2–3 ml. before the end-point.

Notes: (1) The indicator correction of −0.015 ml. of 0.1*N* ferrous solution can usually be ignored when the indicator is added before the dichromate solution. If the indicator is added immediately before the titration, a correction of +0.07 ml. must be taken into consideration. (In the former case, the dichromate and, in the latter, the manganic complex oxidizes the indicator.)

(2) The amounts of metaphosphoric acid, dichromate, and arsenite solution which are added are:

0.08 g. Mn requires 5 g. HPO_3, 35 ml. $K_2Cr_2O_7$, 40 ml. As_2O_3
0.2 g. Mn requires 8 g. HPO_3, 60 ml. $K_2Cr_2O_7$, 65 ml. As_2O_3
0.25 g. Mn requires 10 g. HPO_3, 75 ml. $K_2Cr_2O_7$, 80 ml. As_2O_3

(3) Sodium chloride up to 0.5 g. does not affect the results; in the presence of 1–10 g. the error is proportional to the chloride concentration. Magnesium, calcium, aluminum, nickel, cobalt, lead, copper, tin, and tungsten do not interfere. In the presence of tungstate, diphenylaminesulfonic acid should be used instead of diphenylamine as indicator (see p. 172).

(4) Small amounts of ferric iron do not interfere but large amounts interfere by forming an insoluble metaphosphate complex. Preferably, not more than 0.6 g. of iron should be present because larger amounts yield a precipitate; 10 parts of metaphosphoric acid should be present for each part of iron. Ferrous iron is oxidized to ferric in the procedure. According to Lang, the method gives excellent results for the determination of manganese in steels.

Lang and Kurtz[11] described a modification of the silver-persulfate method based on the work of Travers,[12] who had found that no manganese dioxide separated out during the oxidation in presence of metaphosphoric acid.

Procedure: To 200 ml. of the manganese solution, which is about 0.5*N* in sulfuric acid, add 10 g. of syrupy metaphosphoric acid, 3–5 ml. of 0.1*N* silver nitrate, and 2 g. of potassium persulfate dissolved in water. Boil the mixture for 25 minutes and then cool. Titrate the permanganate formed with 0.1*N* ferrous sulfate solution, adding several drops of 0.1 per cent diphenylamine as indicator near the end-point.

[11] R. Lang and F. Kurtz, *Z. anal. Chem.*, **85**, 181 (1931).
[12] A. Travers, *Compt. rend.*, **182**, 1088 (1926).

Notes: Lang and Kurtz[11] use the method for the determination of manganese in iron.
(2) The substitution of orthophosphoric acid for metaphosphoric acid is not permissible because the permanganate then decomposes to give low values.

Cerium: Cerium can be determined by a procedure similar to that described for manganese (p. 604).[13] The cerous-ceric system has a higher oxidation potential than that of the manganese couple, but the potential is considerably reduced by the formation of a soluble complex with metaphosphoric acid.

Procedure: Dilute the cerous solution containing 5–30 ml. of concentrated hydrochloric acid, 3–40 ml. of concentrated sulfuric acid or 5–50 ml. of nitric acid (sp. gr. 1.40) to 200 ml. with water and add 4–5 g. of metaphosphoric acid dissolved in 10–20 ml. of water. Add 3 drops (0.1 ml.) of 1 per cent diphenylamine solution (or its sulfonic acid). While shaking, add sufficient (see Note 1) dichromate solution (15 g. of potassium dichromate per liter) and arsenite solution (15 g. of arsenic trioxide and 10 g. of sodium carbonate per liter) and rinse down the walls of the flask. After 30 seconds titrate the deep blue solution with $0.1N$ ferrous sulfate (containing 10 ml. of sulfuric acid per liter) until the color changes to green.

Notes: (1) For less than 0.35 g. of cerium, use 30 ml. of dichromate and 35–40 ml. of arsenite solution; for up to 0.63 g. of cerium, use 50 ml. of dichromate and 55–60 ml. of arsenite.
(2) The indicator correction is -0.015 ml. of $0.1N$ ferrous solution. If the indicator is added immediately before the titration, the correction is $+0.07$ ml.

Cerium, Manganese, Chromium, and Vanadium in Presence of Each Other: Lang and Faude[14] have described methods for this determination which are based on selective oxidations with persulfate and with dichromate-arsenite. Manganese and cerium are determined by oxidizing first with persulfate, and the permanganate and cerium(IV) formed are titrated with ferrous solution (titer I). Then the solution is oxidized with dichromate-arsenite so that manganese(III) and cerium(IV) are formed; these ions are then titrated with ferrous solution (titer II) The respective amounts of each constituent can then be calculated. Similar selective oxidations can be applied to the determinations of vanadium and chromium (see below).

Procedure. Manganese and Cerium: To the mixed chloride-free solution containing about 5 ml. of concentrated sulfuric acid, add 6–10 g. of dissolved metaphosphoric acid, 2 g. of potassium persulfate and 2–3 ml. of $0.1N$ silver nitrate. Dilute to 200 ml. and boil for 20 minutes, taking care that the volume does not decrease to less than 150 ml. (glass beads). During the heating, ceric metaphosphate usually separates out. After boiling, add more metaphosphoric acid until the tetravalent cerium is again completely in solution. Cool and titrate with

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[13] R. Lang, *Z. anal. Chem.*, **97**, 395 (1934).

[14] R. Lang and E. Faude, *Z. anal. Chem.*, **108**, 181 (1937).

$0.1N$ ferrous sulfate (in N sulfuric acid) until a rose color develops; then add 3 drops of diphenylamine, diphenylaminesulfonic acid, or ferroin as indicator, and titrate to the end-point. Immediately, add 55 ml. of $0.3N$ potassium dichromate and 60 ml. of $0.3N$ arsenite solution while shaking, and after 30 seconds titrate again with $0.1N$ ferrous solution. For the first titration the indicator correction is +0.07 ml. and for the second, −0.015 ml. of $0.1N$ ferrous solution.

If $0.1N$ ferrous solution is used, the results are calculated as follows:

$$\text{g. Mn} = \frac{(\text{I–II})\ 54.93}{40{,}000} \quad \text{and} \quad \text{g. Ce} = \left(\text{II} - \frac{\text{I–II}}{4}\right)\frac{140.1}{10{,}000}$$

Vanadium and Manganese: These constituents are determined in the same way as manganese and cerium.[15]

Cerium, Manganese, Chromium, and Vanadium: The four metals are titrated with ferrous solution after oxidation to cerium(IV), permanganate, chromate, and vanadate, respectively, by persulfate in presence of silver ions (titer I). Induced oxidation with dichromate and arsenic trioxide and titration with ferrous solution give the sum of cerium(IV), manganese(III), and vanadate (titer II). In a second aliquot of the solution, vanadyl salt is selectively oxidized by excess of permanganate; this is removed with arsenious oxide, osmic acid acting as catalyst,[16] and the vanadate is titrated with ferrous sulfate (titer III). Finally the silver salt-persulfate method is used, whereupon the ceric and permanganate ions are reduced by boiling after the addition of hydrochloric acid. The sum of dichromate and vanadate is then titrated with ferrous solution (titer IV). The original paper should be consulted for further details of procedure and calculation.

Permanganate and Dichromate Mixtures: For the determination of dichromate and permanganate in admixture Rao and Muralikrishna[17] recommended titrating the permanganate with oxalic acid at room temperature in the presence of manganous sulfate catalyst, and subsequently titrating the dichromate with a solution of Mohr's salt.

Procedure: Transfer the solution to an Erlenmeyer flask, add 10 ml. of 1 : 1 sulfuric acid and 2 ml. of $0.025M$ manganous sulfate, and dilute to about 100 ml. with water. Titrate with a standard oxalic acid solution until the brownish red color of the mixture changes to a deep yellow. The amount of permanganate present is calculated from this titer.

Now add 5 ml. of syrupy phosphoric acid and titrate with a standard solution of Mohr's salt. Near the end of the titration add 0.5 ml. of a 0.1 per cent solution of diphenylbenzidine in concentrated sulfuric acid and continue the titration until the blue color is just discharged.

Note: The method was used for amounts of potassium permanganate and dichromate ranging from 3.5 to 33.7 mg. and 3.2 to 56.7 mg., respectively. The accuracy was not affected by wide variations in the ratios of the salts.

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[15] Cf. R. Lang and F. Kurtz, *Z. anal. Chem.*, 86, 288 (1931).

[16] Cf. K. Gleu, *Z. anal. Chem.*, 95, 305 (1933); cf. p. 44.

[17] G. G. Rao and U. Muralikrishna, *Anal. Chim. Acta*, 13, 8 (1955).

Vanadium: Vanadate can be titrated with ferrous sulfate using diphenylamine,[18] diphenylbenzidine,[19] or diphenylaminesulfonic acid[20] as indicator. Ferroin can also be used as indicator;[21] in this case the solution must be $5M$ in sulfuric acid, for at lower acidities the end-point appears too early. The oxidation potential of a vanadate-vanadyl solution is greatly increased by increasing hydrogen-ion concentration, while that of the indicator system is much less affected. Potentiometric titration shows that at the potential at which all the vanadate in $5M$ sulfuric acid solution is quantitatively reduced, 30 per cent of the indicator is reduced. Even at this concentration of the reduced indicator its red color can be observed in the presence of the intense blue color of vanadyl ions.

$$VO_4^{3-} + Fe^{2+} + 6H^+ \longrightarrow VO^{2+} + Fe^{3+} + 3H_2O$$

Procedure: To 25–50 ml. of the vanadate solution, add 100 ml. of 10 M sulfuric acid and dilute to 200 ml. Cool to room temperature, add 1 drop of $0.025M$ ferroin, and titrate with $0.1N$ ferrous sulfate in $1M$ sulfuric acid solution until the color changes from greenish blue to reddish green.

The method can be applied to the determination of vanadium in presence of chromium. To 25–50 ml. of vanadyl solution containing chromic ions, add 4 ml. of $10M$ sulfuric acid. Add $0.1N$ permanganate dropwise until the solution remains rose-colored for 2 minutes. Then add $0.5M$ sodium nitrite dropwise until the permanganate color disappears, followed by 5 g. of urea and 100 ml. of $10M$ sulfuric acid.[22] Dilute to 200 ml. and proceed as above.

Notes: (1) The end-point of the titration is still sharp in the titration of very dilute vanadate solutions with $0.01N$ reagents. It is preferable, however, to add an excess of ferrous sulfate solution and back-titrate with $0.01N$ ceric sulfate solution until the red color of the indicator has disappeared. An indicator correction at the same acidity must be determined. The titration with $0.01N$ solutions can also be done accurately in the presence of 2 g. of iron if sufficient phosphoric acid is added to bleach the color of the iron. Up to 2 per cent of chromium does not interfere.

(2) *N*-Phenylanthranilic acid[23] and variamine blue[24] have also been used as indicators.

[18] N. H. Furman, *Science*, **59**, 560 (1924); *Ind. Eng. Chem.*, **17**, 314 (1925); cf. K. Someya, *Z. anorg. Chem.*, **139**, 237 (1924); **152**, 391 (1926).

[19] H. H. Willard and P. Young, *Ind. Eng. Chem.*, **20**, 764 (1928).

[20] L. A. Sarver and I. M. Kolthoff, *J. Am. Chem. Soc.*, **53**, 2906 (1931).

[21] G. H. Walden, L. P. Hammett, and S. M. Edmonds, *J. Am. Chem. Soc.*, **56**, 57 (1934).

[22] R. Lang and F. Kurtz, *Z. anal. Chem.*, **86**, 288 (1931).

[23] L. M. Orlova, *Zavodskaya Lab.*, **21**, 29 (1955).

[24] L. Erdey, K. Vigh, and E. Bodor, *Acta Chim. Acad. Sci. Hung.*, **7**, 293 (1955).

(3) Ducret[25] determines vanadate in the presence of chromate as follows:

Procedure: To 25–30 ml. of solution add 9*N* sulfuric acid to give an acidity of approximately 3*N*. Add 5 ml. of phosphoric acid, 4–5 drops of barium diphenylaminesulfonate indicator and titrate with 0.1*N* ferrous sulfate solution. Near the end-point titrate very slowly. This titer gives the sum of chromate and vanadate.

Add an excess of permanganate to give a light permanent color. After 2 minutes add 2 ml. of 1 per cent sodium azide and shake. After 5 minutes add 5 ml. of phosphoric acid, 20 ml. of 25 per cent sulfuric acid, 3–4 drops of indicator and titrate the vanadate as before.

Chromium and Vanadium in Tungsten Steels: Willard and Young[26] have given various procedures for the determination of chromium and vanadium in tungsten steels. The tungsten is kept in solution as the complex fluoride, and chromium and vanadium are oxidized with persulfate, excess of which is then removed by boiling. The permanganate formed is reduced with sodium azide or nitrite; excess of the latter is destroyed with urea.

Procedure: To 1 g. of steel in a 600 ml. beaker add 25–30 ml. of water and 5 ml. of sulfuric acid (sp. gr. 1.83). Warm carefully until the steel has decomposed and the tungsten has separated as a black powder. Stir and rub to bring all the tungsten into suspension, and add to the boiling solution 5 ml. of 48 per cent hydrofluoric acid and then slowly 5 ml. of nitric acid (sp. gr. 1.42). Boil for 2 minutes, when a clear green solution should be obtained; if not, boil for a further few minutes. Dilute to 300 ml., warm to at least 60°, and add 10 ml. of 0.25 per cent silver nitrate solution and 5 g. of ammonium persulfate. Boil strongly for 10 minutes. The permanganate formed can be removed by either of the following methods.

(*a*) Add dropwise 0.1*M* sodium azide solution to the boiling solution until reduction is complete, and add 1–2 drops in excess. The excess of azide can be decomposed by boiling for 1–2 minutes.

(*b*) Add 0.05*M* sodium nitrite solution in the same way as above. To decompose the slight excess, add 1 g. of urea and stir well.

Cool the solution to room temperature, add 3 ml. of hydrofluoric acid and 0.3 ml. of indicator solution (a suspension of the oxidized form of diphenylaminesulfonic acid, p. 175) and titrate with 0.05*N* ferrous sulfate. The solution is at first yellowish brown and alters in the titration to purple red and then to purple. The end-point is very sharp from purple to green. Deduct an indicator blank of —0.3 ml. of 0.05*N* solution.

Standardization of Ferrous Sulfate: Transfer 35–50 ml. of 0.05*N* potassium dichromate to a 600 ml. beaker and add 5 ml. of sulfuric acid (sp. gr. 1.5) and 5 ml. of phosphoric acid (sp. gr. 1.37). Dilute with water to 300 ml., add 0.3 ml. of indicator suspension, and titrate with $0.05N$ ferrous sulfate. Use the result without an indicator correction for the calculation of the ferrous titer.

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[25] L. Ducret, *Anal. Chim. Acta,* 1, 135 (1947).

[26] H. H. Willard and P. Young, *Ind. Eng. Chem., Anal. Ed.*, 5, 154, 158 (1933); cf. *Ind. Eng. Chem.*, 20, 764 (1928); *Ind. Eng. Chem., Anal. Ed.*, 4, 187 (1932).

Note: Several alternatives to this procedure have been described, details of which should be sought in the appropriate textbooks of metallurgical analysis.

Chloride: Leithe[27] determines micro and submicro amounts of chloride by precipitating with a standard silver solution. The excess of the latter is precipitated with standard chromate solution and the residual chromate in the filtrate is titrated with a ferrous solution in the presence of diphenylaminesulfonic acid indicator. The method appears to be less attractive than the alternative methods which are available.

Nitrate: When a solution of ferrous sulfate in sulfuric acid is added to a solution of nitrate in strong sulfuric acid, the nitrate is reduced first to nitrite which reacts with sulfuric acid to form nitrosyl sulfuric acid.

$$2FeSO_4 + HNO_3 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + HNO_2 + H_2O$$

$$HNO_2 + H_2SO_4 \longrightarrow H(NO)SO_4 + H_2O$$

When the nitrate has been completely reduced to nitrite the following reaction occurs:

$$2FeSO_4 + 2H(NO)SO_4 \longrightarrow Fe_2(SO_4)_3 \cdot 2NO + H_2SO_4$$

The ferric nitrosyl complex has a rose-red color. Szebellédy[28] has based a titrimetric determination of nitrate on these phenomena. The procedure is less desirable than those described on pp. 183 and 184.

Reagent. 0.1N Ferrous sulfate in 1:2 sulfuric acid: The strongly acidic solution is very sensitive to atmospheric oxidation. It is therefore recommended that air be removed with bicarbonate and that the reagent be stored under an atmosphere of carbon dioxide in order to avoid the need for frequent standardization.

Standardization with Pure Potassium Nitrate: Weigh out about 0.1 g. of pure potassium nitrate and moisten with 10–15 drops of distilled water; dissolve carefully in 50 ml. of concentrated sulfuric acid. (If the sample is large or if more than 20 ml. of titrant is needed, 75 ml. of acid should be used.) After all the salt has dissolved, add about 1 g. of potassium bicarbonate in moderately sized pieces so that the gas development is not too vigorous. Titrate with the ferrous solution while shaking strongly. Cool the solution after about 5 ml. of titrant has been added. The mixture is at first colorless, then becomes greenish yellow, and finally changes to salmon pink; if the solution is slightly overtitrated this turns to carmine red. It is advisable to use a comparison solution, for the end-point is not very easy to see. The end-point is clearer if the solution is thoroughly cooled.

Procedure: Follow the above method for test solutions. Use less than 0.1 g. of nitrate. The following corrections should be used.

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[27] W. Leithe, *Mikrochemie*, **33**, 167 (1947).

[28] L. Szebellédy, *Z. anal. Chem.*, **73**, 145 (1928); cf. W. W. Bowman and F. C. Scott, *Ind. Eng. Chem.*, **7**, 766 (1915); W. D. Treadwell and H. Vontobel, *Helv. Chim. Acta*, **20**, 573 (1937).

Ml. titrant	5	10	15	20	25	30
Correction (mg. of nitrate)	−0.6	−0.4	−0.2	0.0	+0.2	+0.4

Notes: (1) Sulfate, borate, phosphate, and perchlorate do not interfere. Chloride and bromide interfere but can be removed with a suspension of silver sulfate.

(2) Szebellédy[29] also studied the interference of various cations. Alkali and alkaline earth metals, aluminum, manganese(II), zinc, antimony(III), silver, cadmium, and arsenate have no effect on the titration. Lead, mercury(II), bismuth, and barium salts cause the formation of a white precipitate; it is advisable to use a corresponding comparison solution. This should also be done if copper or nickel salts are present. The end-point of the titration cannot be observed in the presence of cobalt and chromic salts. Mercurous salts must be oxidized before the titration.

(3) Johnson[30] uses a similar procedure for the determination of nitrates in sodium nitrite. Nitrite is converted to nitrososulfuric acid before the start of the titration.

TITANOUS CHLORIDE AND SULFATE

Titanous salts are energetic reductants but have the disadvantage that they are very easily attacked by atmospheric oxygen. A standard solution of titanous ion must therefore be carefully protected from air and kept under an inert atmosphere. For this reason, titanous solutions are unsuitable for occasional single determinations, but are of great service in series analyses.

The reducing properties of titanous solutions have long been known,[31] but Knecht and Hibbert[32] were the first to apply the reduction in titrimetric analysis. The procedures are particularly important in the analysis of dyestuffs and in the analysis of organic nitro compounds. Details of the many possible applications have been described in the monograph of Knecht and Hibbert;[33] here we will confine ourselves to the more important methods.

The oxidation potential of the titanous/titanic couple is as follows:

$$\mathrm{Ti^{3+} + H_2O \rightleftharpoons TiO^{2+} + 2H^+ + \mathit{e}} \qquad E^0 = 0.1 \text{ v.}$$

Hydrogen ions are involved in the oxidation and the potential of the system is strongly dependent on the acidity of the solution. Kolthoff[34] found the following value at room temperature:

$$E_{\mathrm{H}} = +0.03 + 0.058 \log \frac{[\mathrm{Ti^{4+}}][\mathrm{H^+}]}{[\mathrm{Ti^{3+}}]} \quad (18°\mathrm{C.})$$

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[29] L. Szebellédy, *Z. anal. Chem.*, **74**, 232 (1928).

[30] C. L. Johnson, *Anal. Chem.*, **25**, 1276 (1953).

[31] Cf. Ebelmen, *J. prakt. Chem.*, 42, 70 (1847); *Jahresber*, **1847/48**, 402.

[32] E. Knecht and E. Hibbert, *Ber.*, 36, 1549 (1903).

[33] E. Knecht and E. Hibbert, *New Reduction Methods in Volumetric Analysis*, 2nd ed., Longmans, Green, London, 1925.

[34] I. M. Kolthoff, *Rec. trav. chim.*, **43**, 768 (1924).

The smaller the hydrogen-ion concentration, the greater is the reducing power. In slightly acid solution and especially in alkaline solution, hydrogen ion itself is reduced to gaseous hydrogen,[35] particularly at boiling temperatures.

$$2H^+ + 2Ti^{3+} \longrightarrow 2Ti^{4+} + H_2$$

This is a great disadvantage in determinations where an excess of titrant is used in a hot solution and is later back-titrated; the error cannot be exactly determined in a blank determination. Kolthoff and Robinson[36] made use of the complex formation with citrate or tartrate. In the presence of these complexing agents, the titanous system becomes much more strongly reducing and many reductions can be carried out at room temperatures.

Both titanous chloride in a hydrochloric acid medium and sulfate in a sulfuric medium have been used as titrants. Lamond[37] prefers the chloride because it is less muddy when partly oxidized than the commercial sulfate which obscures the meniscus and fouls the burette; the iron content of the chloride is usually lower.

The commercial solution of titanous chloride is sold as a dark violet 15–20 per cent solution; this usually contains considerable amounts of ferrous iron which can be tested for by boiling with nitric acid and then adding thiocyanate.[38]

Preparation of Solution: Boil 50 ml. of the commercial 20 per cent solution for 1 minute with 100 ml. of 25 per cent hydrochloric acid, cool, and dilute to 2.25 liters with boiled-out water.

Lamond[37] recommended two procedures for purifying titanous chloride from traces of iron. In one he precipitates $TiCl_3 \cdot 6H_2O$ from the ice-cold solution with hydrochloric acid gas,[39] and in the other he removes iron by extracting as the ferrithiocyanate complex with amyl alcohol-ethyl ether. The latter method is quicker but yields less stable solutions. Titanous sulfate is prepared from the chloride by the addition of excess sulfuric acid; most of the hydrochloric acid is removed by boiling.

Various other preparations of titanium have been proposed. Roseman and Thornton[40] recommended potassium titanium oxalate, $K_2TiO(C_2O_4)_2 \cdot 2H_2O$. The compound is purified by two or three crystallizations and converted to titanic sulfate by digestion with sulfuric acid and ammonium sulfate. The solution is then reduced with zinc or zinc amalgam or preferably by electrolysis.

Wagner *et al.*[41] used titanium hydride, which is said to have a negligibly small iron content. A solution of titanous sulfate is prepared as follows.

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[35] Cf. B. Diethelm and F. Foerster, *Z. physik. Chem.*, 62, 129 (1908).

[36] I. M. Kolthoff and C. Robinson, *Rec. trav. chim.*, 46, 169 (1926).

[37] J. J. Lamond, *Anal. Chim. Acta*, 8, 217 (1953).

[38] I. M. Kolthoff and O. Tomíček, *Rec. trav. chim.*, 43, 775 (1924).

[39] E. Polidori, *Z. anorg. Chem.*, 19, 306 (1899).

[40] R. Roseman and W. M. Thornton, *J. Am. Chem. Soc.*, 57, 328 (1935).

[41] C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, 19, 982 (1947).

Preparation of 0.01N Solution: Heat 20 ml. of concentrated sulfuric acid and 80 ml. of water to 70°C. and add 0.6 g. of titanium hydride in small amounts. When the reaction subsides, boil for 2 minutes and pour into 900 ml. of deaerated water. Allow to settle and siphon into a dark bottle filled with carbon dioxide. Store under hydrogen.

Standardization of Titanous Solutions: If the titer of the solution is determined some days after the preparation and if the solution is stored as described on p. 598 (under hydrogen), its titer remains constant for a long time. However, it is best to standardize the solution frequently because of its great sensitivity. Impure solutions decompose more readily than pure preparations.

Titrations must be carried out in absence of oxygen; this is best done by passing a stream of carbon dioxide or nitrogen through the titration flask. The gas must of course be free from air, and this is ensured by passing it through a spiral wash bottle containing a mixture of 10 per cent titanous chloride and sodium citrate, and then washing it with water.

Knecht and Hibbert[32,33] standardized titanous chloride solution against Mohr's salt after oxidation with permanganate, but the method has not found favor because of the variable ferric content of the salt. The most suitable standardization for general purposes seems to be against dichromate in the presence of excess ferric-free ferrous iron.

Procedure: Weigh 3 g. of ferrous ammonium sulfate into a 500 ml. flask. Pass a strong stream of carbon dioxide and add 50 ml. of recently boiled-out water and 25 ml. of 40 per cent sulfuric acid. Add rapidly 40 ml. of 0.1*N* potassium dichromate solution and run in the titanous chloride until near the calculated end-point. Quickly add 5 g. of ammonium thiocyanate and complete the titration to the disappearance of the red color. Determine the blank on 3 g. of Mohr's salt under the same conditions.

Notes: (1) Ferric ammonium sulfate can also be used as standard substance[42] (cf. p. 57), but this salt effloresces readily, so that dichromate must be preferred.

(2) Smith and Getz[2] used potassium ferricyanide or ferrocyanide as reference compound. The sample is first digested with perchloric and sulfuric acids to form ferric perchlorate.

Breit[43] examined several methods for the standardization and found that direct titration of dichromate gave the most consistent results but the values were high because of the iron content of the titanous solution. The titration was done in hydrochloric acid solution with diphenylamine as indicator. Pierson and Gantz[44] recommended a similar method for iron-free solutions prepared from titanium hydride.

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[42] W. M. Thornton and J. E. Chapman, *J. Am. Chem. Soc.*, **43**, 91 (1921).

[43] J. E. Breit, *J. Assoc. Offic. Agr. Chemists*, **30**, 504 (1947); **31**, 573 (1948); **32**, 589 (1949).

Procedure: Pass carbon dioxide through a 300 ml. flask for 3 minutes and add 40 ml. of 0.2*N* potassium dichromate and 80 ml. of 10 per cent sulfuric acid. Titrate with titanous solution and add 4 drops of 0.5 per cent aqueous sodium diphenylbenzidinesulfonate indicator near the end-point. Diphenylaminesulfonic acid and phenylanthranilic acid are also suitable indicators.

Note: Pierson and Gantz give directions for the exact determination of the iron content of titanous solutions. The titer of the solution is determined as above; an aliquot of the titanous solution is oxidized with permanganate, excess of which is removed with ammonium thiocyanate and the ferric iron formed is titrated with the titanous solution under test. The iron content is calculated with the aid of simultaneous equations.

Ferric Iron: The titration of ferric iron with titanous chloride was first described by Knecht;[45] thiocyanate is a suitable indicator, for as soon as all the ferric iron has been reduced the red-brown color of the ferrithiocyanate complex disappears. Thornton and Chapman[46] systematically examined this titration; they found that 1 per cent more titrant is required in the presence of air than when the titration is carried out under carbon dioxide. The dilution of the solution and the concentration of hydrochloric or sulfuric acid are unimportant; nitric acid interferes because it is reduced by titanous salt. Thornton and Chapman recommended titration at below 30°C. in the presence of 10 ml. of 10 per cent potassium thiocyanate. Monnier[47] suggested methylene blue as a suitable indicator; when the ferric iron has been reduced the dye is bleached. In acid solution, sodium tungstate serves the same purpose; tungstate itself is colorless but is reduced by a slight excess of titanous chloride to a blue tungsten compound.

Kolthoff[48] found that at room temperature the last traces of ferric iron are but slowly reduced; 1–2 per cent too much titanous solution is required when thiocyanate is used as indicator. The results are very accurate if the titration is done very slowly near the end-point. The titration may also be done at higher temperatures.

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[44] R. H. Pierson and E. St. C. Gantz, *Anal. Chem.*, **26**, 1809 (1954).

[45] E. Knecht, *Ber.*, **36**, 166 (1903); E. Knecht and E. Hibbert, *ibid.*, **36**, 1549 (1903).

[46] W. M. Thornton and J. E. Chapman, *J. Am. Chem. Soc.*, **43**, 91 (1921); cf. W. M. Thornton and A. E. Wood, *Ind. Eng. Chem.*, 19, 150 (1927).

[47] A. Monnier, *Ann. chim. anal. appl.*, **21**, 109 (1916).

[48] I. M. Kolthoff, *Rec. trav. chim.*, **43**, 816 (1924).

Procedure: To about 50 ml. of ferric solution add 5–10 ml. of 4*N* hydrochloric or sulfuric acid (the exact amount is of no importance), heat to 50–60°C., and add 0.5–1 ml. of 10 per cent potassium thiocyanate solution. Add three portions of about 300 mg. of sodium bicarbonate to drive the air from the solution and titrate with titanous chloride solution. When the color starts to disappear, continue the titration very slowly with strong shaking until the solution is bleached. The accuracy of this procedure is 0.5 per cent. In order to obtain a greater accuracy (0.1–0.2 per cent) lead carbon dioxide through the flask during the titration.

Notes: (1) If methylene blue is used as indicator at room temperatures, the results are about 2 per cent high; at 50–70°C., accurate values are obtained.

(2) Ferric iron can also be titrated with titanous chloride using the intense violet chromic acid compound with diphenylcarbohydrazide as indicator with a copper salt as catalyst.[49]

(3) Titanous chloride is recommended for the determination of iron in aluminium and its alloys in a recent British Standard specification.[50]

(4) Someya[51] recommended diphenylamine as indicator for the titration of chromic acid and ferricyanide; the indicator solution and phosphoric acid are added in the same way as that described by Knop (cf. p. 177). For the titration of ferricyanide, 70–130 ml. of concentrated hydrochloric acid should be present for every 130 ml. of solution.

(5) Columbium may be determined in the presence of tantalum, by first reducing, with amalgamated zinc, oxidizing with a known excess of standard ferric chloride, and back-titrating with standard titanous chloride.[52] Titration of the ferrous iron formed seems much simpler and more accurate.

Cupric Copper: Copper salts are also quantitatively reduced by titanous chloride. Moser[53] titrated to the disappearance of the blue color; with very dilute solutions this method is naturally inexact and an error of 10 per cent or more can occur. Monnier[47] recommended safranine or indulin as indicator. After all the copper has been reduced to the cuprous state, the dyestuff is bleached; however, the reduced forms of these dyestuffs are very sensitive to oxidation and the method is not to be recommended.

The best results are obtained by the method of Rhead,[54] in which thiocyanate and a little ferrous salt are added and the solution is titrated to colorlessness. During the titration, cuprous thiocyanate precipitates and the solution is colored red by the ferrithiocyanate complex; at the end-point, the well-stirred solution becomes white.

[49] L. Brandt, *Stahl u. Eisen*, 46, 976 (1926); see *Z. anal. Chem.*, **70**, 405 (1927).

[50] British Standard, 1728, Pt. 6 (1955).

[51] K. Someya, *Z. anorg. Chem.*, 152, 386 (1926).

[52] V. Schwarz, *Chem. Abstr.*, 46, 2445 (1952).

[53] L. Moser, *Chem. Ztg.*, 36, 1126 (1912).

[54] E. L. Rhead, *J. Chem. Soc.*, 89, 1491 (1906).

This method has been used for the determination of copper in various solutions.[55]

Procedure: Add a little ferrous sulfate and 3–5 ml. of 10 per cent potassium thiocyanate solution to the acidified copper solution, remove most of the air with bicarbonate, and titrate slowly with titanous chloride solution in an atmosphere of carbon dioxide. The accuracy of this method is 0.5 per cent.

Ferric and Cupric Ions in Presence of Each Other: The above procedure allows the sum of cupric and ferric ions to be determined in the presence of thiocyanate. Emmett[56] recommended that the titration be done at room temperature because ferric and cupric thiocyanate rapidly decompose at higher temperatures. If iron alone is to be titrated in presence of copper, Monnier[47] recommended methylene blue as indicator. However, this dyestuff is bleached only after a measurable amount of copper has reacted; the results are therefore inexact.

Kolthoff[48] found that meconic acid was a suitable indicator for the titration; in acid solution, reddish brown ferric meconate is formed. On titration with titanous chloride, the color decreases through orange-brown to yellowish brown and turns pale yellow at the end-point, which is thus less sharp than with thiocyanate; with experience, however, it can be established to 0.03 ml. of $0.1N$ titrant. When copper is present, the color changes from yellowish brown through greenish brown to pale blue: before experience has been gained in the detection of the end-point, it is advisable to use a comparison solution of a previously titrated solution containing a slight excess of titanous ion. For each 50 ml. of solution, 0.5–1 ml. of 0.5 per cent aqueous meconic acid solution should be added. It is best to carry out the titration under carbon dioxide at 50–60°C.; the reduction of the last traces of ferric iron is then much faster and the accuracy of the titration is about 0.4 per cent. After the reduction of the iron, copper can be titrated iodometrically (p. 348).

Note: Most of the metals which generally accompany copper and iron do not interfere. Pentavalent antimony is but slowly reduced by titanous chloride at room temperatures when the acidity of the solution is properly adjusted; the method can thus be applied to the determination of copper and iron in the presence of antimony. All the metals are converted to their highest oxidation states by bromine or bromate-bromide mixture in acid solution; the unconsumed bromine is boiled out. The total amount of copper and iron is determined in an aliquot of the solution with thiocyanate as indicator, and in a second aliquot iron alone is titrated with meconic acid as indicator. Arsenic (III) or (V) does not interfere in these titrations.

Antimony: Holness and Cornish[57] recommend the titration of pentavalent antimony with titanous sulfate.

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[55] F. Mach and P. Lederle, *Landwirtsch. Vers. St.*, 90, 191 (1917); see *Z. anal. Chem.*, 56, 69 (1917); 58, 375 (1919).

[56] W. G. Emmett, *J. Chem. Soc.*, 1927, 2059.

[57] H. Holness and G. Cornish, *Analyst*, 67, 221 (1942).

Procedure: To the solution of antimony in the titration flask add 50 ml. of concentrated hydrochloric acid, 100 ml. of water, and 5 drops of bromine and boil until all the bromine has been removed (10 minutes). Pass carbon dioxide through the flask and titrate in the inert atmosphere with standard titanous solution. When the yellowish color (from traces of iron) vanishes, add 5 drops of aqueous 0.1 per cent indigo carmine solution and titrate dropwise until the blue color disappears; strong daylight or daylight fluorescent lighting should be used. The temperature at the end of the titration should be above 60° C.

Note: The following indicators can also be used as 0.1 per cent solutions: neutral red (blue to colorless), safranine (violet to colorless), phenosafranine (magenta to colorless), and brilliant cresyl blue (green to yellow to colorless). Copper, iron, and arsenic, which are reduced along with antimony, interfere with the titration.

Nitrate: Knecht and Hibbert[33] determined nitrate by treatment with ferrous iron as in the Pelouze method (p. 81). Instead of back-titrating the excess of ferrous iron with permanganate they titrated the ferric iron formed with titanous chloride solution. Wellings[58] described a direct titration in which alizarin (3 ml. of 0.1 per cent ethanolic solution) serves as indicator. The action of the indicator is interesting. In boiling neutral nitrate solution, its color is red; during the titration titanic hydroxide separates out by hydrolysis and adsorbs the red indicator. On further titration a deep grey-green color appears which disappears when the solution is boiled; the red color then returns. The solution must be boiled vigorously after each addition of reagent until the red color no longer returns. The color change may be due to reduction of the adsorbed alizarin.

Oldham[59] described methods for aliphatic nitrates. The compound is boiled for 20 minutes with excess of titanous sulfate, which is then back-titrated with ferric alum; methylene blue is used as indicator. An empirical factor is necessary.

Perchlorate: Perchlorate can be reduced to chloride by boiling for a long time with titanous solution in a strong hydrochloric acid medium.[60] The titrant is not stable under these conditions and the method can give only approximate results. Meldrum *et al.*[61] described a procedure for the determination of perchlorate in smokeless powder in which the reduction is completed in 5 minutes, but the method is not very accurate.

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[58] A. W. Wellings, *Trans. Faraday Soc.*, **28**, 665 (1932).

[59] J. W. H. Oldham, *J. Soc. Chem. Ind.*, **53**, 236T (1934).

[60] V. Rothmund, *Z. anorg. Chem.*, 62, 108 (1909); V. Rothmund and A. Burgstaller, *Chem. Ztg.*, **33**, 1245 (1909); F. König, *Z. anorg. Chem.*, **120**, 48 (1921); E. Spitalsky and S. Jofa, *Z. anorg. Chem.*, **169**, 309 (1928).

[61] W. B. Meldrum, R. A. Clarke, D. L. Kouba, and W. W. Becker, *Anal. Chem.*, **20**, 949 (1948).

Many other oxidizing agents, such as dichromate, ferricyanide, selenious acid, nitrite, hydroxylamine, nitrate, per salts, hydrogen peroxide, chlorate, antimonate, and gold salts, can be determined with titanous solutions. In most cases, the titanous chloride solution is added in excess and back-titrated with a ferric solution with thiocyanate as indicator. The procedures are only of slight practical interest, and the work of Knecht and Hibbert[33] should be consulted for details.

Nitro Compounds: For the determination of nitro groups in aromatic compounds, it is customary to boil in hydrochloric acid solution with excess titanous chloride and to back-titrate with ferric solution. As has been seen (p. 611), this method cannot give exact results because of the reduction of hydrogen ions. Callan *et al.*[62] found that considerable errors can arise from the chlorination of the organic compound; low results are thus obtained. These authors recommend titanous sulfate in sulfuric acid solution as reagent; this is best standardized against *p*-nitroaniline.[63] The reducing power of a titanous chloride solution increases greatly with decreasing hydrogen-ion concentration (p. 611). Kolthoff and Robinson[36] have based a simple method for the determination of nitro groups on this reaction; to lower the acidity, sodium citrate is added. (With Seignette salt, potassium hydrogen tartrate precipitates, but this does not interfere.)

Procedure: To the test solution, add 30 ml. of 20 per cent tertiary sodium citrate and then about 0.25 g. of sodium bicarbonate to drive out air. Pass carbon dioxide, previously washed with titanous solution and citrate solution, through the flask (p. 612). After 3–5 minutes, titrate slowly with titanous chloride solution until the mixture is colored dark violet; the titanous chloride is then present in slight excess (1–3 ml. of 0.1*N*). Continue to pass carbon dioxide through the flask and acidify after 2 minutes with 20 ml. of concentrated hydrochloric acid (sp. gr. 1.18). Add 5 ml. of 10 per cent potassium or ammonium thiocyanate solution and titrate the excess of titanous chloride slowly with standard ferric solution until the red color does not fade for 2 minutes. The thiocyanate should be added after the acid; otherwise it is reduced by titanous chloride.

$$RNO_2 + 6TiCl_3 + 6HCl \longrightarrow RNH_2 + 6TiCl_4 + 2H_2O$$

Notes: (1) One millimole of a mononitro compound consumes 6 equivalents of titanous solution. Thus even a few milligrams can be determined accurately.

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[62] T. Callan, J. A. R. Henderson, and N. Strafford, *J. Soc. Chem. Ind.*, **39**, 86T (1920); T. Callan and J. A. R. Henderson, *ibid.*, **41**, 157T (1922).

[63] Cf. F. L. English, *J. Ind. Eng. Chem.*, **12**, 994 (1920).

(2) Even twice recrystallized sodium citrate consumes a little titanous chloride; about 0.1 ml. of $0.1N$ titanous solution is used by 30 ml. of 20 per cent solution. It is therefore advisable to standardize the titanous solution under the same conditions as in the general determination. *p*-Nitroaniline is a very suitable compound for use as standard, and can easily be purified by recrystallization.

(3) The method can be applied to the determination of *o*-, *m*-, and *p*-nitroaniline, picric acid, nitronaphthalene, *p*- and *o*-nitrophenol, and nitrobenzene. The accuracy is 1 per cent. Under the given conditions there is no evidence for any error from chlorination (cf. Callan *et al.*[62]). Special care should be taken because of the air sensitivity of titanous chloride in the presence of citrate.

(4) For the titration of very volatile nitro compounds, it is best to place the citrate and titanous solutions in the flask with carbon dioxide passing through and then to add a suitable amount of the test solution. The excess of titanous is then titrated as above.

(5) Ethanol has no effect on the titration, so that difficultly soluble compounds can be first dissolved in this solvent.

(6) Neutral salts do not interfere in any way.

(7) Nitroso and azo compounds can often be determined in this way

$$RNO + 4TiCl_3 + 4HCl \longrightarrow RNH_2 + 4TiCl_4 + H_2O$$

$$RN = NR' + 4TiCl_3 + 4HCl \longrightarrow RNH_2 + R'NH_2 + 4TiCl_4$$

(8) Butts *et al.*[64] state that acetate is a more satisfactory buffer than citrate. When 30 ml. of 20 per cent sodium acetate is present, the reduction of dinitrotoluene by titanous chloride is complete in 15 seconds.

(9) Carbonyl groups may be determined[65] by treating the compound with a known excess of 2,4-dinitrophenylhydrazine in slightly hydrochloric acid solution. The insoluble hydrazone precipitates and the excess reagent is determined by reduction with titanous chloride. Methyl glyoxal in the presence of trioses and hexoses can be determined by a similar method.[66]

Nitroglycerin: According to Shankster and Wilde,[67] the reduction of nitroglycerin by titanous chloride proceeds as follows:

$$NO_2OCH(CH_2ONO_2)_2 + 18H^+ + 18Ti^{3+} \longrightarrow 18Ti^{4+} + NH_2OCH(CH_2ONH_2)_2 + 6H_2O$$

Procedure: Dissolve 1 g. of the sample in methanol and dilute to 1 liter with methanol. To 10 ml. of this solution, add 25 ml. of $0.05N$ titanous chloride solution while passing carbon dioxide and boil the solution for 10 minutes after letting stand for 10 minutes. Cool, add thiocyanate, and titrate with standard ferric solution. Run a blank on the methanol used.

Becker[68] reduced nitroglycerin by the method of Huff and Leitsch[69] with ferrous chloride in acetic acid as solvent and titrated the ferric iron formed with titanous chloride solution. The advantage of this method is that it can be applied in the presence of aromatic nitro compounds.

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[64] P. G. Butts, W. J. Meikle, J. Shovers, D. L. Kouba, and W. W. Becker, *Anal. Chem.*, 20, 947 (1948).

[65] W. Schöniger and H. Lieb, *Mikrochemie*, **38**, 165 (1951); W. Schöniger, H. Lieb, and K. Gassner, *Mikrochim. Acta*, **1953**, 434.

[66] V. Prey, E. Waldman, and F. Ludwig, *Monatsh.*, 82, 1022 (1951).

[67] H. Shankster and T. H. Wilde, *J. Soc. Chem. Ind.*, **57**, 91 (1938).

[68] W. W. Becker, *Ind. Eng. Chem., Anal. Ed.*, 5, 152 (1933); cf. I. S. Hirschhorn, *Anal. Chem.*, **19**, 880 (1947).

[69] W. J. Huff and R. D. Leitsch, *J. Am. Chem. Soc.*, **44**, 2643 (1922).

Procedure: Dissolve 1.8–2.0 g. of nitroglycerin in glacial acetic acid and dilute to the mark in a 250 ml. graduated flask. Transfer 25 ml. of this solution to the titration flask, remove the air with carbon dioxide, and add 15 ml. of 0.7*N* ferrous chloride solution in 0.6*N* hydrochloric acid. Add 25 ml. of 1:1 hydrochloric acid. Boil under reflux for 5 minutes, during which time carbon dioxide is passed. Cool while still passing carbon dioxide and titrate with titanous chloride solution with 5 ml. of 20 per cent thiocyanate solution as indicator. Run a blank determination for the amount of ferric iron in the reagent.

Notes: (1) Shaefer and Becker[70] have applied a similar method to the determination of nitrocellulose in lacquers.

(2) It would be simpler to titrate the excess of ferrous iron with ceric sulfate.

Nitroguanidine: The reduction of nitroguanidine and its derivatives has recently been subjected to much study. Kouba *et al.*[71] recommended boiling for 15 minutes, but Sternglanz *et al.*[72] were unable to confirm their results; they suggested that the boiling time was at fault. With a minimum of 200 per cent excess of titanous chloride in a weakly acid citrate-containing solution the reduction is quantitative at room temperature. Six equivalents of titanous solution are required.

Procedure: Dissolve 1.2–2.4 meq. of sample in 10 ml. of 10 per cent acetic acid (or in glacial acetic acid and later dilute with water). Displace air with powdered carbon dioxide and then maintain a stream of carbon dioxide. Heat to room temperature, add 10 ml. of potassium citrate solution (containing 800 g. per liter) and excess of 0.3*N* titanous chloride. Stir for 3 minutes, add 20 ml. of 1:1 hydrochloric acid, and 5 ml. of 0.25 per cent ammonium thiocyanate and titrate with 0.1*N* ferric alum solution in the usual way.

Notes: (1) Brandt *et al.*[73] found that reduction was better with a mixture of titanous and ferrous solutions. The iron is said to complex an intermediate hydroxyl compound, rendering it liable to further reaction; 8 equivalents of titanous are required.

(2) Stalcup and Williams[74] determined nitrocellulose by transnitration of salicylic acid. The nitrosalicylic acid is then reduced with excess of titanous chloride, which is titrated with ferric alum solution. The method is said to be very accurate.

Organic Peroxides: Yule and Wilson[75] preferred to reduce organic peroxides with ferrous thiocyanate in aqueous acetone and to titrate the ferric iron formed with titanous solution rather than to use the more common methods. The procedure is much more sensitive then the Kokatnur-Jelling method (p. 398) but is quite empirical. Wagner *et al.*[76]

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[70] W. E. Shaefer and W. W. Becker, *Anal. Chem.*, 25, 1226 (1953).

[71] D. L. Kouba, R. C. Kicklighter, and W. W. Becker, *Anal. Chem.*, 20, 948 (1948); cf. R. P. Zimmermann and E. Lieber, *ibid.*, 22, 1151 (1950).

[72] P. D. Sternglanz, R. C. Thompson, and W. L. Savell, *Anal. Chem.*, 25, 1111 (1953).

[73] W. W. Brandt, J. E. DeVries, and E. St. C. Gantz, *Anal. Chem.*, 27, 392 (1955).

[74] H. Stalcup and R. W. Williams, *Anal. Chem.*, 27, 543 (1955).

[75] J. A. C. Yule and C. P. Wilson, *Ind. Eng. Chem.*, 23, 1254 (1931).

[76] C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, 19, 982 (1947)

have investigated its application to many autoxidized hydrocarbons and organic peroxides. The results obtained, although precise, were generally only fractions of the true values. The method appears much less accurate than the iodometric procedure.

Sulfoxides: Barnard and Hargrave[77] found the reduction with titanous chloride to be the most satisfactory of several methods which they examined for the determination of sulfoxides. Two procedures were described depending on the saturation of the compound.

Procedure. Saturated Sulfoxides: Dissolve 0.7–1 meq. of the compound in 10 ml. of glacial acetic acid and evacuate the flask to a pressure of 20 mm. Add 15 ml. of $0.1N$ titanous chloride and repeat the evacuation twice. Immerse the flask to one third of its height in a water bath at 80°C. for 1 hour. Add a boiling solution of 5 ml. of ferric alum (see Note 1) in 50 ml. of water, allow to stand for 30 seconds, and then cool rapidly. Add 10 ml. of phosphoric acid solution and 15 ml. of carbon tetrachloride. Shake thoroughly and titrate with $0.05N$ dichromate solution, using diphenylaminesulfonic acid as indicator. Run a blank on the solvent.

$$\% \text{ sulfoxide} = \frac{(\text{blank} - \text{titer}) \times N \text{ dichromate} \times \text{mol. wt. of sulfoxide} \times 100}{2000 \times \text{sample weight}}$$

Notes: (1) The indicator, phosphoric acid and ferric alum solutions are the same as those described for the determination of peroxides (see p. 186).

(2) Thioethers are always present with sulfoxides and would interfere were they not extracted into the organic solvent layer before the titration. If alcohols are present, it is better to titrate the titanous excess directly with ferric alum solution. Sulfones, disulfides, ketones, and compounds containing ethylenic double bonds do not interfere, but nitro, azo, and diazo compounds and hydroperoxides interfere.

(3) The reduction is usually complete in 10–15 minutes at 80°C., but the time can be extended to several hours without altering the accuracy of the method.

(4) Since commercial titanous solutions contain ferrous iron, it would be necessary to standardize the solution in the same manner as in the procedure.

The above procedure gives only 80–95 per cent recoveries with unsaturated sulfoxides. However, if 1.5 ml. of $3M$ ammonium thiocyanate is added before the titanous solution, satisfactory results are obtained. The excess of titanous chloride is titrated in the usual way with $0.05N$ ferric alum solution under nitrogen. The catalytic action of thiocyanate is probably due to its forming a complex with sulfoxide which precipitates and redissolves during the course of the titration.

Barnard and Hargrave[78] also describe the determination of mixtures of peroxides and sulfoxides by a combination of the above method with that described for peroxides (p. 186).

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[77] D. Barnard and K. R. Hargrave, *Anal. Chim. Acta,* **5**, 536 (1951).

[78] D. Barnard and K. R. Hargrave, *Anal. Chim. Acta,* **6**, 23 (1952).

Quinone: Quinone can be directly reduced in acid solution to hydroquinone by titanous chloride:

$$C_6H_4O_2 + 2TiCl_3 + 2HCl \longrightarrow C_6H_4O_2H_2 + 2TiCl_4$$

Methylene blue is a suitable indicator.[33]

Dyestuffs which form colorless leuco compounds can be titrated directly with titanous chloride until they are bleached, e.g., methylene blue, indigo sulfonate, acid fuchsin, magenta, eosin (in presence of 50 per cent ethanol), malachite green, rhodamine, aniline blue, safranine (in presence of sodium bitartrate).

In general, the best results are obtained when considerable amounts of Seignette's salt or sodium acetate are added (3–5 g.)[79] before titrating with titanous solution.

Methylene blue is reduced in the following way:

$$C_{16}H_{18}N_3SCl + H_2 \longrightarrow \underset{\text{colorless leuco compound}}{C_{16}H_{20}N_3SCl}$$

Details of these determinations should be sought in the monograph of Knecht and Hibbert.[33]

STANNOUS CHLORIDE

Stannous chloride was the first titrant to be used for the direct titration of ferric iron.[80] It has been recommended again in recent times,[81] and its applications have been extended.[82] The oxidation potential of the system is as follows:

$$Sn^{2+} \rightleftharpoons Sn^{4+} + 2e \qquad E^0 = 0.14 \text{ v.}$$

but is strongly dependent on the pH of the solution. Szabó and Sugar[82] have described a simple apparatus for the storage of standard stannous solutions (p. 598, Fig. 2); after the solution has reached equilibrium (in about 5 days), there is no necessity for a daily check on the standardization.

Preparation of 0.1N Solution: Place 80 ml. of concentrated hydrochloric acid per liter of final solution in the storage bottle and add 4–5 g. of calcium carbonate to expel all air from the acid and the bottle. Rapidly weigh the required amount of crystalline stannous chloride (12 g. per liter), dissolve in the acid, and dilute with boiled-out distilled water. Evolution of carbon dioxide should continue throughout the preparation. Maintain an atmosphere of carbon dioxide by placing the stopper in position as in Fig. 2.

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[79] Cf. O. L. Evenson, *J. Assoc. Offic. Agr. Chemists*, 27, 370 (1944).

[80] R. Fresenius, *Z. anal. Chem.*, 1, 26, 32 (1862).

[81] Z. G. Szabó and E. Sugar, *Anal. Chem.*, 22, 361 (1950).

[82] *Idem, Anal. Chim. Acta*, 6, 293 (1952).

Standardization of Solution: The solution may be standardized against potassium bromate using rubrophen (p. 505) as indicator or against potassium iodate.

Procedure: Add 2 ml. of concentrated hydrochloric acid to 20 ml. of standard 0.1N potassium iodate solution and titrate immediately with the stannous solution; add starch as indicator near the end-point. An atmosphere of carbon dioxide is said to be unnecessary if the titration is done quickly.

Ferric Iron:[81,82] The reduction of ferric iron with stannous solution can be used for direct titration of iron (cf. p. 187). The reaction is very rapid at 60–70°C. if the initial solution is 0.25–1.6N in hydrochloric acid. Chlorostannite ions are thought to be the active agent, so that a large excess of chloride salt is also added. A double indicator is used to show the end-point. The reduction of most of the ferric iron is observed by the fading of the thiocyanate complex color; ammonium molybdate and phosphate are then added and the end-point is finally shown by the formation of molybdenum blue when a slight excess of stannous ion is present.

Procedure: Transfer 20 ml. of the ferric chloride solution containing 3–150 mg. of iron to a 100 ml. narrow-necked flask and add 2 ml. of concentrated hydrochloric acid and 1 g. of ammonium chloride. Heat to 60–70°C. and maintain this temperature throughout the titration. Add a few marble chips to provide an inert atmosphere, and 2–3 drops of 0.1N potassium thiocyanate as indicator. Titrate with 0.1N stannous chloride solution until a straw-yellow color appears. Add 1–2 drops of 0.1N disodium hydrogen phosphate and 5–6 drops of saturated ammonium molybdate solution and titrate further to the color change from green to pale blue.

Notes: (1) More than small amounts of copper or chromic ions obscure the end-point. Aluminum, manganese, zinc, lead, silver, arsenate, arsenite, and antimony(V) do not interfere. Sulfate solutions can be titrated so long as plenty of chloride is present.

(2) Kuchment and Gengrinovitch[83] use 1 ml. of saturated cacotheline solution and titrate the boiling ferric solution, which is 2N in hydrochloric acid, to the appearance of a violet color.

Other Determinations: Dichromate and vanadate[82] can be titrated with stannous solution at room temperatures in about 3–3.5N hydrochloric acid, diphenylamine serving as indicator; an atmosphere of carbon dioxide is essential. It is possible to titrate vanadium(V) first and then to determine ferric iron by the above procedure. Vanadium(V) can also be titrated using ammonium molybdate as external indicator.[84] Nitrate can be determined by reduction with ferrous ammonium sulfate in alkaline solution in the presence of silver diammine sulfate (cf. p. 185); the ferric iron formed is titrated with stannous tin solution.[85] The original papers should be consulted for details.

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[83] M. L. Kuchment and A. I. Gengrinovitch, *Zavodskaya Lab.*, 11, 267 (1945).

MERCUROUS NITRATE

Ferric Iron: Bradbury and Edwards[86] have suggested the use of mercurous nitrate as a reagent for the titration of ferric iron. They noted that in the presence of an excess of thiocyanate, ferric iron was quantitatively reduced by mercury(I) and the end-point was marked by the disappearance of the colored ferrithiocyanate complex.

The great advantage of this titrant is that it is stable indefinitely without requiring any special precautions for its storage. No other known titrant for ferric iron has this property.

A more detailed examination of this reaction was made by Belcher and West[87] and by Burriel and Lucena.[88] The reaction was shown to be stoichiometric. The mechanism appears to be due to a shift in the usual potentials of the systems involved, owing to the complexing action of thiocyanate ions. Belcher and West[89] showed that the reaction could be predicted thermodynamically and may be formulated

$$Hg_2^{2+} + 2(Fe(CNS)_6)^{3-} \rightleftharpoons 2Fe^{2+} + 2(Hg(CNS)_4)^{2-} + 4CNS^-$$

and $K = 1.3 \times 10^{-21}$.

The reducing properties of this system are dependent on two distinct factors, i.e., the formation of the mercurithiocyanate complex and of the ferrithiocyanate complex. Accordingly, mercury(I) does not possess enhanced reducing powers unless both thiocyanate and ferric ions are present to take part in the reaction.

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[84] Warynski and Mdivani, *Bull. soc. chim. France,* (4) 3, 626 (1908).

[85] Z. G. Szabó, L. Bartha, and J. S. Fiala, *Acta Chim. Acad. Sci. Hung.,* 3, 231 (1953).

[86] F. R. Bradbury and E. G. Edwards, *J. Soc. Chem. Ind.,* 59, 96T (1940).

[87] R. Belcher and T. S. West, *Anal. Chim. Acta,* 5, 260, 268, 472 (1951).

[88] F. M. Burriel and F. C. Lucena, *Anales real soc. españ. fís. y quím. (Madrid),* 47B, 257 (1951); 49B, 45 (1953).

[89] R. Belcher and T. S. West, *Anal. Chim. Acta,* 7, 470 (1952).

Interferences are remarkably few; hydrochloric acid interferes when the concentration is above $0.8N$ but the effect may be minimized by increasing the amount of thiocyanate. Nitric acid should not exceed $2.5N$, nor sulfuric acid $3.8N$.

Copper interferes at all concentrations (p. 625). Strong reductants (e.g., tin(II)) or strong oxidants (e.g., cerium(IV)) interfere, respectively by reducing the ferric iron originally present, or by oxidizing the ferrous iron formed during the reaction. Thallium, bismuth, molybdate, selenite, fluoride, oxalate, and pyrophosphate interfere. In some cases the interferences can be eliminated.

The reagent has been examined by other investigators.[90] Pugh[91] prefers mercurous perchlorate but there is little to choose between the two forms of the reagent.[87]

Preparation of $0.1N$ Mercurous Nitrate: Weigh slightly more than the theoretical amount of mercurous nitrate and dissolve in $0.5N$ nitric acid. The solution is stable indefinitely without any precautions being taken to prevent atmospheric oxidation.

Standardization: Weigh an appropriate amount of ferric alum, dissolve in $0.5N$ nitric acid, and proceed as in the determination of iron given below.

Procedure for Determination of Ferric Iron:[87] Transfer the solution, which should be about $0.5N$ in nitric acid, to a 250 ml. Erlenmeyer flask. Add 10 ml. of 40 per cent ammonium thiocyanate solution and sufficient $0.5N$ nitric acid so that the volume is approximately 100 ml. at the end-point. Titrate with standard mercurous nitrate until the blood-red color fades to orange. Continue the titration dropwise, shaking well and allowing 15 seconds between each drop until the last trace of color disappears.

Notes: (1) It is important to titrate slowly once the color fades to orange. A too rapid addition causes a turbidity because of the formation of mercurous thiocyanate. When this occurs the determination should be discarded.

(2) Ten milliliters of 40 per cent thiocyanate solution will suffice for up to 100 mg. of iron. For larger amounts 1 ml. extra should be added for each 10 mg. of iron; excess of thiocyanate has no adverse effect.

(3) Orthophosphate retards the reaction but does not interfere. Fluoride, pyrophosphate, and oxalate bleach the color of the ferrithiocyanate complex, but their effect may be minimized by increasing the concentration of nitric acid. Care must be taken, however, not to exceed $2.5N$; the end-point is much more sluggish under these conditions. Nitrite interferes but can be removed by adding a slight excess of sulfamic acid, warming and then cooling before the titration.

(4) The method gives an accuracy of about 0.4 per cent.

(5) The procedure has been applied to the analysis of ores.[92]

[90] S. A. Babushkin and M. L. Pogrebinskaya, *Zavodskaya lab.*, **14**, 1182 (1948); cf. H. Flaschka, *Mikrochemie*, **35**, 473 (1950); F. R. Bradbury, K. C. Chattergee, and E. G. Edwards, *Quart. J. Pharm.*, **13**, 297 (1940); R. Belcher and C. E. Spooner, *Fuel*, **20**, 172 (1941).

[91] W. Pugh, *J. Chem. Soc.*, **1945**, 588.

[92] D. N. Finkel'shtein and G. N. Kryuchkova, *Zavodskaya Lab.*, **21**, 403 (1955).

Copper: In the presence of an excess of thiocyanate, copper(II) is reduced to copper(I) by ferrous salts. This is a reversal of the usual reaction and is due to the potentials of the systems involved being altered by complex formation.[93] The ferric iron produced which is titrated with mercurous nitrate is thus a direct measure of the cupric salt originally present.

Procedure: To the solution containing copper add an excess of ferrous ammonium sulfate solution and 10 ml. of 40 per cent ammonium thiocyanate for every 20 ml. of $0.1M$ copper sulfate. Add sufficient nitric acid to bring the normality to $0.5N$. Titrate with mercurous nitrate solution, following exactly the procedure used for the determination of ferric iron.

Note: The reducing action of ferrous iron under these conditions has also been applied to the gravimetric determination of copper as cuprous thiocyanate.[94]

Other Determinations: Several oxidizing agents may be determined by adding an excess of ferrous ammonium sulfate and titrating the ferric iron formed. For example, dichromate, permanganate, cerium (IV), vanadate, persulfate, and chlorate may be determined in this way.[95] Although no particular advantage is gained by titrating compounds such as permanganate or dichromate in this way, the reactions offer a useful alternative means of standardizing the titrant.

Hydroxylamine may be determined by boiling with an excess of standard ferric alum solution and back-titrating the cool solution.[96] Mercury(I) may be determined similarly except that the reaction is carried out at room temperature.[97] Appreciable quantities of mercury(II) may be present.

The reducing action of mercury(I) as the perchlorate in an alkaline medium has also been studied.[98] In the presence of iodide, ferricyanide can be titrated accurately; the end-point may be determined potentiometrically or by the use of barium diphenylaminesulfonate as indicator. Chromium(III), arsenite, hydrogen peroxide, and hydrazine may be determined by oxidizing with a standard solution of ferricyanide and back-titrating with mercurous perchlorate.

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[93] R. Belcher and T. S. West, *Anal. Chim. Acta*, 5, 364 (1951).

[94] R. Belcher and T. S. West, *Anal. Chim. Acta*, 6, 337 (1952).

[95] R. Belcher, and T. S. West, *Anal. Chim. Acta*, 5, 360 (1951); cf. V. M. Tarayan, *Referativnyi Zhur. Khim.*, 1955, 14216, 14230, 14264.

[96] R. Belcher and T. S. West, *Anal. Chim. Acta*, 5, 546 (1951).

[97] *Idem, ibid.*, 474.

[98] F. M. Burriel, F. C. Lucena, and S. J. Arribas, *Anal. Chim. Acta*, **10**, 301 (1954); **11**, 214 (1954).

ASCORBIC ACID

The use of ascorbic acid as a titrant is based on its reduction to dehydroascorbic acid according to the following equation:[99]

$$C_6H_8O_6 \rightleftharpoons C_6H_6O_6 + 2H^+ + 2e$$

Erdey and Bodor state that the redox potential of this reaction at pH 7 is +0.185 v. at 21 °C.,[100] but Rao and Rao[101] claim that the redox potential varies from −0.012 v. at pH 8.7 to +0.326 v. at pH 1.05. The reactions are carried out in acidic solutions; in alkaline solutions dehydroascorbic acid is more readily oxidized.

The most important application of ascorbic acid is to the direct titration of ferric iron,[99,100] for the titrant appears to be more stable than most other powerful reducing agents.

Stability of Solution: If prepared with twice-distilled water, a 0.1*N* solution is stable for about 24 hours and its titer decreases daily by about 0.3 per cent.[100] Traces of heavy metals,[100] enzymes of the oxidase type, and ultraviolet light[101] strongly catalyze the decomposition, which also depends on the purity of the ascorbic acid used. Erdey and Bodor[100] found that when the solution is kept in a Winkler-type tank burette under carbon dioxide, its titer decreases for two days and remains constant for a further two weeks. These authors later stated[102] that ethylenediaminetetraacetic acid and formic acid can be used to stabilize the solutions and an inert atmosphere is unnecessary. A 0.1*N* solution containing 0.1 g. of EDTA and 4 g. of formic acid per liter loses only 0.1 per cent of its titer daily; a solution containing 0.5 g. of EDTA per liter and no formic acid is stable for a long time when stored at 0°C. out of direct sunlight. The action of EDTA must be attributed to the formation of stable complexes with heavy metals.

Flaschka and Zavagyl[103] found that the instability increases with increasing dilution. They stabilized 0.01*N* solutions by adding 10 per cent of ammonium thiocyanate. When kept in the dark, the solution lost only 1 per cent of its titer in 30 days. Rao and Rao[101] found that oxalic or sulfuric acid exerted a slight beneficial effect on the stability.

Preparation of 0.1*N* Solution: Weigh 8.806 g. of pure ascorbic acid, dissolve in metal-free water, and dilute to 1 liter. Either add one of the stabilizers mentioned above before dilution or store under carbon dioxide.

Standardization: The solution may be standardized against Mohr's salt after oxidation with hydrogen peroxide,[103] but the use of iodate or iodine is more convenient.[100]

Procedure: Add 1 g. of potassium iodide to 20 ml. of 0.1*N* potassium iodate (p. 456), acidify with 5 ml. of 2*N* hydrochloric acid, and titrate with the ascorbic acid solution to the disappearance of the iodine color. Starch is not added since it is said to decrease the reaction rate.[104]

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[99] L. Erdey, *Magyar Kém. Folyoirat*, **56**, 262 (1950).

[100] L. Erdey and E. Bodor, *Anal. Chem.*, **24**, 418 (1952).

[101] G. G. Rao and V. N. Rao, *Z. anal. Chem.*, **147**, 338 (1955).

[102] L. Erdey and E. Bodor, *Magyar Kém. Folyoirat*, **58**, 295 (1952).

[103] H. Flaschka and H. Zavagyl, *Z. anal. Chem.*, **132**, 170 (1951).

[104] Cf. G. G. Rao and V. N. Rao, *Z. anal. Chem.*, **147**, 338 (1955).

Ferric Iron: Ferric iron can be titrated directly in 0.1–0.2*N* hydrochloric acid solution, thiocyanate being used to detect the end-point by the disappearance of the red color of the ferric complex.[99,100] The reduction tends to be slow at room temperature and the titration is best done at about 50°C. Above 60°C., dehydroascorbic acid may also be oxidized. Flaschka and Zavagyl[103] state that the method gives exact results. They used thiocyanate to stabilize the titrant, which was also 0.1*N* in hydrochloric acid, and no further addition of indicator was required.

Procedure: To the nearly neutral solution containing 25–250 mg. of iron add 5 ml. of 2*N* hydrochloric acid and sufficient water so that the volume at the end-point will be between 50 and 100 ml. Heat to below 60°C., add 1 ml. of 0.5*N* potassium thiocyanate solution, and titrate with 0.1*N* ascorbic acid solution until the solution becomes colorless. Complete the titration within 5 minutes.

Notes: (1) Atmospheric oxygen does not affect the titration if it is completed within 5 minutes. Strong oxidants naturally interfere, but small amounts of free nitric acid and large amounts of nitrate can be tolerated. Sulfate does not interfere, but large amounts of phosphate and even small quantities of fluoride cause fading end-points and incomplete reduction of the ferric complex. In colored solutions the end-point may be determined electrometrically.[100] The method has been applied to ores and bauxites. Ferrous iron can be easily oxidized with hydrogen peroxide.[100,103]

(2) Erdey and Bodor[105] later recommended variamine blue (4-amino-4′-methoxydiphenylamine) as indicator in the above titration; it is said to be much better than thiocyanate. The titration is carried out under the previous conditions except that 0.1–0.2 ml. of a 1 per cent solution of the indicator is added just before the end-point, which is then reversible; the indicator is destroyed in strong oxidizing media. Salicylic acid or sulfosalicylic acid can also be used as indicator.[106]

(3) The titration has been applied in the indirect determination of vanadium[107] and of oxygen in water.[108] Ferrous solution is added to the test solution and the ferric iron formed is determined.

Other Determinations: Under the correct conditions, *silver* salts are reduced to metallic silver by ascorbic acid. This has been made the

$$2AgNO_3 + C_6H_8O_6 \longrightarrow 2Ag + C_6H_6O_6 + 2HNO_3$$

basis of a simple determination of silver.[109] The reduction is slow at room temperature but is quite rapid at 60°C.; at 80°C. dehydroascorbic acid is also attacked. The end-point can be determined potentiometrically or visually with the aid of variamine blue. It is said to be more accurate than the Volhard method, although the average deviation of the results is similar. The Mohr and Fajans methods are inferior in both accuracy and precision.

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[105] L. Erdey and A. Bodor, *Z. anal. Chem.*, **137**, 410 (1953).

[106] L. Erdey and E. Bodor, *Z. anal. Chem.*, **133**, 265 (1951).

[107] L. Erdey, E. Bodor, and I. Buzás, *Acta Chim. Acad. Sci. Hung.*, **7**, 277, 287 (1955); cf. C. Yoshimura and T. Fuzitani, *J. Chem. Soc. Japan*, **76**, 305 (1955).

[108] L. Erdey and F. Szabadváry, *Acta Chim. Acad. Sci. Hung.*, **4**, 325 (1954).

[109] L. Erdey and I. Buzás, *Acta Chim. Acad. Sci. Hung.*, **4**, 195 (1954).

The method can be applied to the determination of silver in alloys, coins, cyanide baths, and waste fixing solutions.[109]

Gold and *platinum* salts may be determined by reduction to the metal in the same way as silver.[106] *Mercuric salts* may be determined by a procedure similar to that for silver salts.[110] The original papers should be consulted for details.

Chlorate, bromate, and *iodate* can be determined by direct titration with ascorbic acid solution.[111] The procedures for bromate and iodate are of little practical value, but that for chlorate is interesting in that it is one of the few direct titrations available for this anion. Selenious acid is added to catalyze the reaction which is carried out in 4*N* sulfuric acid medium at 60°C. The end-point is shown by the separation of colloidal selenium, and manganous sulfate is added to retard reduction of selenious acid during the titration. The titration is more sensitive when mercuric chloride is added; the precipitation of mercurous chloride then marks the end-point.

Ascorbic acid solution can also be used instead of thiosulfate in a wide variety of iodometric determinations;[112] variamine blue serves as indicator (cf. p. 212). The methods are only of academic interest.

VANADIUM IN ITS LOWER VALENCY FORMS

Hypovanadous Salts: Russell[113] proposed hypovanadous sulfate ($VSO_4 \cdot 7H_2O$) as a reducing titrant. It is a more powerful reductant than titanous sulfate and has several applications; the oxidation potential is as follows:

$$V^{2+} \longrightarrow V^{3+} + e \qquad E^0 = -0.2 \text{ v.}$$

Thus the reducing power lies between those of chromous and titanous solutions.

Russell averred that a 0.1*N* solution in 10*N* sulfuric acid is not measurably oxidized when kept in an open burette for 1 hour. However, since later investigators stress the necessity for maintaining the usual precautions which are adopted with vigorous reductants of this type, it may be concluded that significant errors could arise under Russell's conditions.

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[110] L. Erdey and I. Buzás, *Acta Chim. Acad. Sci. Hung.*, **8**, 263 (1955); cf. G. G. Rao and U. V. Rao, *Z. anal. Chem.*, **150**, 29 (1956).

[111] L. Erdey and A. Bodor, *Z. anal. Chem.*, **133**, 265 (1951); L. Erdey, A. Bodor, and H. Buzás, *ibid.*, **134**, 22, 142 (1951).

[112] L. Erdey, E. Bodor, and M. Papay, *Acta Chim. Acad. Sci. Hung.*, **5**, 235 (1955).

[113] A. S. Russell, *J. Chem. Soc.*, **1926**, 497.

Banerjee[114] prepared hypovanadous ammonium sulfate, which is more stable than hypovanadous sulfate, by electrolytic reduction of vanadyl sulfate in presence of ammonium sulfate. He stored the solution under the usual reducing conditions and titrated in an atmosphere of carbon dioxide at 90–100°C. Yoshida[115] used zinc amalgam to prepare hypovanadoussulfate from vanadate.

Maass[114] titrated various metals with hypovanadous solutions potentiometrically, but Banerjee[114] used visual methods. He titrated iron in the presence of thiocyanate as indicator and standardized the vanadium(II) solution in this way against ferric alum.

Several other determinations have been described. For example, chlorates, nitrate, and persulfates have been reduced with excess of vanadium(II), which was back-titrated with permanganate.[115,116] Many of the other methods,[117] however, appear to be of little practical value because the particular ions to which they apply can be determined more readily by other means.

Various nitro compounds may be determined by boiling them with an excess of hypovanadous solution and back-titrating with standard ferric alum solution in the presence of ammonium thiocyanate as indicator.[118] The procedure is said to be as accurate as the reduction with titanous salts but appears to offer no advantage.

Vanadous Salts: Salts of trivalent vanadium have been used for a limited number of determinations.[119] Manganese (VII), chromium(VI), and vanadium(V) have been determined by titrating with the vanadium(III) solution in the presence of *N*-phenylanthranilic acid as indicator. The method has been applied to the analysis of ores. It appears to be of little practical importance.

Vanadyl Solutions ($(VO)^{2+}$): Vanadyl sulfate ($VOSO_4$) can be prepared from ammonium vanadate by reducing with sulfur dioxide, the excess of which is removed by passing carbon dioxide. The acid solution is stable in air. In an alkaline medium (in which it is generally used), atmospheric oxidation is rapid and it is necessary to maintain an inert atmosphere.

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[114] P. C. Banerjee, *J. Indian Chem. Soc.*, 12, 198 (1935); cf. K. Maass, *Z. anal Chem.*, 97, 241 (1934).

[115] Y. Yoshida, *J. Chem. Soc. Japan*, 59, 49 (1938).

[116] P. C. Banerjee, *J. Indian Chem. Soc.*, 13, 301 (1936).

[117] P. C. Banerjee, *J. Indian Chem. Soc.*, 15, 475 (1938); 19, 30 (1942).

[118] P. C. Banerjee, *J. Indian Chem. Soc.*, 19, 35 (1942); cf. O. G. Sheĭntsis, *Zavodskaya Lab.*, 10, 151 (1944).

[119] V. S. Syrokomskiĭ and K. N. Zhukova, *Zavodskaya Lab.*, 11, 754 (1945).

Several determinations in an alkaline medium were reported by del Fresno *et al.*,[120] who reduced chromate, permanganate, ferricyanide, copper, gold, and silver. The end-points were determined potentiometrically in all cases. Willard and Manalo[121] examined several diphenylamine derivatives as indicators in the titration of ferricyanide with vanadyl sulfate; they recommended 2-carboxy-2 -methoxydiphenylamine as the most suitable. They determined arsenite, antimonite, chromium, hydrazine sulfate, and hydrogen peroxide by oxidizing with an excess of ferricyanide in an alkaline medium at 85–90°C. and back-titrating with vanadyl sulfate at room temperature.

Vanadyl sulfate has been used in an acid medium for the titration of permanganate[122] and Caro's acid.[123]

CHROMOUS SALTS

Systematic studies on the use of chromous solutions for the direct potentiometric titration of certain metals were first undertaken by Zintl and his coworkers.[124] Occasional applications had been made by earlier investigators.[125] Someya[126] determined chlorate and nitro compounds by reducing with an excess of chromous chloride and back-titrating with a ferric solution; he used thiocyanate as indicator, following the usual procedure for titanous solutions.

The oxidation potential of the chromous-chromic system is as follows:[127]

$$Cr^{2+} \longrightarrow Cr^{3+} + e \qquad E^0 = -0.41 \text{ v.}$$

it is the most powerful reductant used as a titrant. The titration of several metals successively in the presence of each other is possible. In nearly every application of chromous solutions as titrants the end-point is determined potentiometrically; hence a detailed description of the methods is outside the scope of this text. The few applications where visual end-points are used are relatively unimportant.

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[120] C. del Fresno and E. Mairlot, *Anales soc. españ. fís y quím.* (*Madrid*), **30**, 254 (1932); **31**, 122, 531 (1933); **32**, 28 (1934); *Z. anorg. Chem.*, **214**, 73 (1933); C. del Fresno and E. de Lafuente, *Gazz. chim. ital.*, **68**, 619 (1938).

[121] H. H. Willard and G. D. Manalo, *Ind. Eng. Chem., Anal. Ed.*, **19**, 167 (1947).

[122] I. Tsubaki and M. Kiura, *Japan. Analyst*, **3**, 137 (1954).

[123] A. J. Berry, *Analyst*, **58**, 464 (1933).

[124] E. Zintl and coworkers, *Z. anorg. Chem.*, **139**, 397 (1925); **155**, 84 (1926); **161**, 374, 385 (1927); **168**, 97 (1928): cf. *Z. angew Chem.*, **40**, 1286 (1927); **41**, 956 (1928). A full review of the literature is given by E. Brennecke, *Newer Methods of Volumetric Chemical Analysis*, W. Böttger, ed., Chapman and Hall, London, 1938, p. 129; cf. H. C. Jerschkewitz and G. Rienäcker, *Neuere Massanalytischen Methoden*, 6th ed., G. Jander, ed., Enke, Stuttgart, 1956, pp. 186–250.

[125] O. Dimroth and F. Frister, *Ber.*, **55**, 3693 (1922); T. F. Buehrer and O. E. Schupp, *Ind. Eng. Chem.*, **18**, 121 (1926).

[126] K. Someya, *Z. anorg. Chem.*, **160**, 355 (1927).

[127] G. Grube and G. Brintzinger, *Z. Elektrochem.*, **33**, 112 (1927).

In more recent times there appears to be a newly aroused interest in this titrant and several workers have described its preparation and storage. The original papers should be consulted for further details of preparation and storage,[128] visual determinations of dissolved oxygen in water,[129] of chloroform and of carbon tetrachloride,[130] and potentiometric determination of various organic compounds.[131] Pallaud[132] has discussed the advantages of chromium(II) over titanium(III) as a reducing agent.

MISCELLANEOUS REDUCING TITRANTS

There is considerable information in the literature concerning the titration of uranium(IV) with oxidizing agents, but only limited use has been made of quadrivalent uranium as a titrant. Vortmann and Binder[133] first used uranous sulfate for the titration of nitrate, chlorate, chromate, manganese dioxide, and ferric iron. Only the last substance was determined directly, i.e., by titration to the disappearance of the color of ferrithiocyanate. The other oxidants were determined either by adding an excess of ferrous sulfate and titrating the ferric iron produced with uranous sulfate, or by adding an excess of uranous sulfate and back-titrating with ferric iron.

This work was extended by later investigators. Belcher, Gibbons, and West[134] titrated several substances potentiometrically, but they concluded that methods involving the use of this titrant are less convenient and hold no advantage over more conventional methods. The end-points are generally sluggish unless the titrations are done at elevated temperatures. More recently Issa and Sherif[135] have titrated several oxidizing agents with uranous sulfate potentiometrically at room temperature, but they were unable to overcome the slowness of reaction even under the most favorable conditions of acidity or with catalysts present. Accordingly it may be taken that their results support the observations of Belcher *et al.* that this titrant is only of academic interest.

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[128] H. W. Stone and C. Beeson, *Ind. Eng. Chem., Anal. Ed.*, **8**, 88 (1936); R. Flatt and F. Sommer, *Helv. Chim. Acta*, **25**, 684 (1942); **27**, 1518, 1522 (1944); J. J. Lingane and R. L. Pecsok, *Anal. Chem.*, **20**, 425 (1948); I. Muraki, *J. Chem. Soc. Japan*, **71**, 407 (1950); **72**, 376 (1951).

[129] H. W. Stone and R. L. Eichelberger, *Anal. Chem.*, **33**, 868 (1951).

[130] T. Kiba and K. Terada, *J. Chem. Soc. Japan*, **75**, 196 (1954).

[131] R. S. Bottei and N. H. Furman, *Anal. Chem.*, **27**, 1182 (1955).

[132] R. Pallaud, *Chim. anal.*, **33**, 181 (1951).

[133] G. Vortmann and F. Binder, *Z. anal. Chem.*, **67**, 269 (1925).

[134] R. Belcher, D. Gibbons, and T. S. West, *Anal. Chem.*, **26**, 1025 (1954).

[135] I. M. Issa and I. M. El Sherif, *Anal. Chim. Acta*, **14**, 466 (1956).

Various other titrants have been used: e.g., thallium(I),[136] molybdenum-(V)[137], tungsten(V)[138], tungsten(III)[139], cuprous ethylenediaminetetraacetic acid,[140] and ferrous ethylenediaminetetraacetic acid.[141]

Most of the methods which use these reagents depend on potentiometric determination of the end-point; visual end-points are possible only in a limited number of cases. The reagents appear to be mainly of academic interest and details of their use should be sought in the original literature.

[136] U. V. Rao, U. Muralikrishna, and G. G. Rao, *Z. anal. Chem.*, **145**, 12 (1955); cf. I. M. Issa and R. M. Issa, *Anal. Chim. Acta*, **13**, 23 (1955); I. M. Issa and I. M. El Sherif, *ibid.*, **14**, 300 (1956).

[137] A. R. Tourky, M. Y. Farah, and H. K. El Shamy, *Analyst*, **73**, 258, 266 (1948).

[138] A. R. Tourky, I. M. Issa, and A. M. Amin, *Anal. Chim. Acta*, **10**, 168 (1954).

[139] R. Uzel and R. Přibil, *Collection Czech Chem. Communs.*, **10**, 330 (1938).

[140] R. Belcher, D. Gibbons, and T. S. West, *Anal. Chim. Acta*, **12**, 107 (1955).

[141] R. Přibil, V. Simon, and J. Doležal, *Collection Czech Chem. Communs.*, **16**, 573 (1951).

CHAPTER XV

MISCELLANEOUS TITRANTS

1. Oxidizing Titrants.

VANADIUM(V)

Vanadium in the di-, tri-, tetra-, and pentavalent states has been employed as a titrant in a great variety of methods (cf. p. 628). The pentavalent form is by far the most important in titrimetry and it has received some considerable attention in recent years.

The molal potential of the vanadate-vanadyl system is +1.00 v. at 22° C. and increases from 1.02 v. in $1M$ to 1.30 v. in $8M$ sulfuric acid.[1] Syrokomskii and Antropov[2] found that the following relationship was valid:

$$E = E_0' + 0.0173\,(N\ H_2SO_4) \qquad E_0' = 0.97\text{ v.}$$

The oxidizing power of vanadate is thus akin to that of dichromate; as with the latter, the titration of iron is the most important of the reactions.

Vanadium(V) appears to have been first recommended as a titrant by two independent groups of investigators. Syrokomskii and Stiepin[3] titrated ferrous iron with ammonium vanadate and used *N*-phenylanthranilic acid as indicator. At about the same time, Lang and Gottlieb[4] described a method for the determination of molybdenum after reduction to molybdenum(V); they titrated with ammonium vanadate solution in the presence of diphenylamine or its sulfonic acid as indicator. The first systematic examination of the titrant was not published until 1938.[5]

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[1] H. H. Willard and G. D. Manalo, *Ind. Eng. Chem., Anal. Ed.*, 19, 462 (1947).

[2] V. S. Syrokomskii and L. I. Antropov, *Zavodskaya Lab.*, 9, 818 (1940).

[3] V. S. Syrokomskii and V. V. Stiepin, *Zavodskaya Lab.*, 5, 144 (1936); cf. *J. Am. Chem. Soc.*, 58, 928 (1936).

[4] R. Lang and S. Gottlieb, *Z. anal. Chem.*, 104, 1 (1936).

[5] V. S. Syrokomskii and Y. V. Klimenko, *Zavodskaya Lab.*, 7, 1093 (1938).

Preparation of Solutions: Ammonium vanadate and sodium metavanadate can both be used as titrants. Recrystallized and dried ammonium vanadate is said to be a primary standard,[6] but the solution is generally standardized before use. A 0.1*N* solution is prepared by weighing out about 12 g. of the salt and dissolving it in 80 ml. of 1:1 sulfuric acid before dilution to 1 liter.[4] Sodium vanadate solution can be prepared by dissolving the required amount of ammonium vanadate in water and boiling with a slight excess of sodium carbonate until free from ammonia; after cooling, the solution is diluted to 1 liter. This preparation is stable for several months.[7]

Standardization of Solutions: Vanadate solutions are commonly standardized against a standard solution of Mohr's salt and thus indirectly against dichromate.

West and Skoog[8] used primary standard sodium oxalate. Although oxalate is not oxidized by vanadate at moderate acidities, it is decomposed by excess of vanadate in solutions containing more than 50 per cent of sulfuric acid. The heat of dilution is sufficient to ensure complete reaction. A 0.3*N* solution of ammonium vanadate has been standardized in this way.

Procedure: Transfer 0.1–0.2 g. of primary standard sodium oxalate to a 250 ml. Erlenmeyer flask and add 10 ml. of 0.3*N* vanadate solution containing 100 ml. of concentrated sulfuric acid per liter. Add 25 ml. of concentrated sulfuric acid and swirl cautiously. After 3–10 minutes, dilute with 100 ml. of water and allow to cool to room temperature. Titrate with 0.1*N* ferrous ammonium sulfate solution until the blue color of the vanadyl ion is distinct. Add 3–5 drops of 0.066*M* *N*-phenylanthranilic acid solution as indicator and titrate slowly to the color change from purple to green. Determine the volume ratio of the vanadate to the ferrous iron solution.

$$2VO_3^- + H_2C_2O_4 + 6H^+ \longrightarrow 2VO^{2+} + 2CO_2 + 4H_2O$$

Note: The method is slightly less accurate than standardization against Mohr's salt solution which has been checked against dichromate.

Methods for Determination of Compounds. ***Ferrous Iron:*** The titration of ferrous iron with vanadate is satisfactory in 4–13.5*N* sulfuric acid media when *N*-phenylanthranilic acid is used as reversible indicator;[2] the results agree well with the potentiometric titration. Satisfactory results can be obtained even with 0.002*N* vanadate solutions.[9] A ferrous solution which is up to 4*N* in hydrochloric acid may be titrated accurately; thus vanadate is even less affected by this acid than potassium dichromate (cf. p. 177).

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[6] E. Bishop and A. B. Crawford, *Analyst*, 75, 273 (1950).

[7] V. P. Rao, B. V. S. R. Murty, and G. G. Rao, *Z. anal. Chem.*, 147, 161 (1955).

[8] D. M. West and D. A. Skoog, *Anal. Chim. Acta*, 12, 301 (1955).

[9] V. V. Stiepin, *Zavodskaya Lab.*, 8, 262 (1939).

Organic compounds have less influence on the titration than when dichromate or cerium(IV) is used as titrant. For example, phenols and alcohols do not interfere.[10] High results are obtained when saccharated ferrous carbonate is titrated with dichromate, but titration with vanadate is satisfactory.[6] In this case, barium diphenylaminesulfonate is used as indicator in the presence of phosphoric acid; a sharp end-point is obtained only if a slight excess of vanadate is added and then titrated back with standard ferrous solution.

Note: Platinum[11] and palladium[12] may be determined by reduction with excess of standard ferrous and back-titration with a vanadate solution. Insoluble chloroplatinates and chloropalladates may be determined likewise.

Ferric Iron: Ferric iron can be titrated with vanadate after reduction in the Jones reductor. The solution should be 0.5–1N in sulfuric acid during the titration; diphenylamine, diphenylbenzidine, or diphenylaminesulfonate is used as indicator in the presence of 10 ml. of phosphoric acid, and a little oxalic acid is added to sharpen the end-point, which is otherwise rather sluggish.[13] The reduction can also be done with oxalic acid in ultraviolet light[13,14] but this is only of academic interest. The vanadate titration can also be applied to solutions after reduction with hypophosphite (cf. p. 151).[15]

Syrokomskii and Zhukova[16] determined iron in technical acids and alkalis by reduction of ferric iron with chromous solution. After the excess chromous has been oxidized by air the ferrous iron is titrated with 0.002N vanadate solution. Ores can be analyzed after suitable treatment.[17]

Molybdenum: Pentavalent molybdenum can be readily titrated with vanadate solutions. Molybdate solutions can be reduced with excess stannous chloride,[4] but the procedure is very involved and the original paper should be consulted for details. Mercury can be used for the reduction in 2–3N hydrochloric acid (cf. p. 153) and the molybdenum(V) solution is titrated with 0.1N ammonium vanadate in the presence of N-phenylanthranilic acid as indicator. The molybdate solution can also be titrated after passage through a bismuth reductor; the solution should be 1–1.5N in hydrochloric acid, for at higher acidities some molybdenum(III) is also formed.[18] Molybdenum(VI) is reduced to the trivalent state by zinc amalgam. The titration of trivalent molybdenum with vanadate has been applied to the indirect determination of phosphate,[3] calcium, and lead.[19]

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[10] G. G. Rao, J. V. S. Ramanjaneyulu, and M. N. Sastri, *Current Sci. (India)*, **18**, 72, 169 (1949).

[11] V. S. Syrokomskii and N. N. Proshenkova, *Zhur. Anal. Khim.*, **1**, 83 (1946).

[12] V. S. Syrokomskii and S. M. Gubel'bank, *ibid.*, **4**, 146 (1949).

[13] G. G. Rao, G. Aravamudan, and N. C. Venkatamma, *Z. anal. Chem.*, **146**, 161 (1955).

[14] Cf. M. N. Sastri and C. Kalidas, *Z. anal. Chem.*, **149**, 181 (1956).

[15] M. N. Sastri and C. R. K. Murty, *Z. anal. Chem.*, **147**, 16 (1955).

[16] V. S. Syrokomskii and K. N. Zhukova, *Zavodskaya Lab.*, **11**, 373 (1945).

[17] T. Ikegami, O. Kammori, and S. Morita, *Chem. Abstr.*, **49**, 7445 (1955).

Uranium: Several methods have been described for the determination of uranium after reduction to the quadrivalent state, by titration with vanadate. The first application appears to be due to Syrokomskii and Klimenko,[19] but details of the procedure are not available. They used *N*-phenylanthranilic acid as indicator. Rao and his coworkers[20] used diphenylbenzidine but found it necessary to catalyze the reaction with oxalic acid; later phosphoric acid was also used. *N*-Phenylanthranilic acid was satisfactory as indicator provided that the acid concentration was in excess of 5*N*; oxalic acid catalyst was also necessary.

Procedure: To 10–25 ml. of about 0.05*N* uranium(IV) solution (obtained by passage through a Jones reductor; see p. 189) add 10 ml. of 10*N* sulfuric acid, 2 ml. of 1*M* oxalic acid, 5 ml. of syrupy phosphoric acid, and 0.5 ml. of 0.1 per cent diphenylbenzidine. Dilute to 100 ml. and titrate with 0.05*N* vanadate solution while stirring well.

Notes: (1) If desired, 1–2 drops of 0.1 per cent *N*-phenylanthranilic acid may be used as indicator. In this case, add 40 ml. of 10*N* sulfuric acid and omit the phosphoric acid.

(2) Rao *et al.*[21] also photochemically reduce uranium with ethanol. It is claimed that the reduction is stayed at the uranium(IV) stage and no uranium(III) is produced.

Sulfur Compounds.

Sulfite: Lang and Kurtenacker[22] determined sulfite by oxidizing to sulfate with a hot solution of vanadic acid and titrating the vanadyl salt with permanganate. Rao and Rao[23] described a simpler process in which the oxidation is done at room temperature in the presence of iodine monochloride catalyst.

[18] E. V. Ankudimova, *Chem. Abstr.*, **49,** 12187 (1955); cf. K. Saito, *ibid.*, **47,** 1007 (1953).

[19] V. S. Syrokomskii and Y. V. Klimenko, *Zavodskaya Lab.*, **9,** 1077 (1940)

[20] M. N. Sastri and G. G. Rao, *Current Sci.* (*India*), **18,** 402 (1949); V. P Rao, B. V. S. R. Murty, and G. G. Rao, *Z. anal. Chem.*, **147,** 161 (1955).

[21] G. G. Rao, V. P. Rao, and N. C. Venkatamma, *Z. anal. Chem.*, **150,** 178 (1956).

[22] R. Lang and H. Kurtenacker, *Z. anal. Chem.*, **123,** 169 (1942).

[23] K. B. Rao and G. G. Rao, *Anal. Chim. Acta*, **13,** 320 (1955).

Procedure: Add the sulfite solution to a slight excess of vanadate solution containing hydrochloric acid to give a final acidity of 5*N* and 1 ml. of catalyst (p. 132). After 5 minutes, titrate the excess of vanadate with standard Mohr's salt solution. *N*-phenylanthranilic acid is used as indicator; diphenylbenzidine is unsuitable.

Thiosulfate: Oxidation to tetrathionate is quantitative in 10 minutes at room temperature if the acidity is above 2.7*N;* or in 2–5 minutes at boiling water bath temperatures if the acidity is above 0.06*N*.[24] However, a positive error is obtained under the latter conditions because some sulfate is formed. When copper is used as catalyst the reaction is complete in 20 minutes at room temperature, even at an acid concentration of 0.05*N*. Since the acidity is critical it is better to use a weak acid such as acetic acid; between concentrations of 2*N* and 8*N*, the time and temperature are not critical with this acid.

Procedure: Allow the thiosulfate solution (0.1–1 millimole of thiosulfate) to flow into an excess of 0.05*N* sodium vanadate containing acetic acid (to give an acid concentration 2–8*N*) and 1 ml. of 1 per cent copper acetate. Dilute to 50 ml. with water. Set aside for 5 minutes, add 5 ml. of phosphoric acid, and back-titrate with standard Mohr's salt. Use diphenylbenzidine as indicator.

Notes: (1) The error for the above amount of thiosulfate is 0 to +0.6 per cent.

(2) Thiosulfate is oxidized quantitatively to sulfate in 10 minutes in 5*N* hydrochloric acid with iodine monochloride as catalyst at room temperature. An alternative procedure based on this reaction has also been described.[24]

Hypophosphite and Phosphite: Rao and Gowda[25] found that both phosphite and hypophosphite were rapidly oxidized by vanadate at elevated temperatures in the presence of silver catalyst. Their recommended conditions for the determination of hypophosphite are not clear but appear to be as follows:

Procedure 1. Hypophosphite: To 10 ml. of approximately 0.01*M* hypophosphite add 20 ml. of 0.05*N* sodium vanadate and concentrated sulfuric acid to give an 8.5–12*N* acid solution. Add 2 ml. of 5 per cent silver sulfate in concentrated sulfuric acid, dilute to 50 ml., and heat for 20 minutes on a boiling water bath. Cool and titrate with 0.05*N* Mohr's salt in the presence of *N*-phenylanthranilic acid as indicator.

In the phosphite determination the acid concentration can vary from 1.25*N* to 7.2*N* without the results being affected. However, as distinct from hypophosphite, increasing the acid concentration above 1.25*N* does not accelerate the reaction.

Procedure 2. Phosphite: Proceed in the same way as for hypophosphite but use 10 ml. of 1 per cent silver sulfate in 3*N* sulfuric acid; the acidity is as stated above.

Other Determinations: Several other determinations are possible, but these are mainly of academic interest. Details should be sought in the original literature. Arsenite,[26] hydrazine,[27] osmium(IV),[28] nickel,[29] and palladium[30] (the last two after precipitation by various organic reagents) may be determined by treatment with an excess of vanadate and back-titration with ferrous sulfate.

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[24] H. S. Gowda, K. B. Rao, and G. G. Rao, *Anal. Chim. Acta,* **12,** 506 (1955); cf. R. Lang and H. Kurtenacker, *Z. anal. Chem.*, **123,** 169 (1942).

[25] G. G. Rao and H. S. Gowda, *Z. anal. Chem.*, **146,** 167 (1955).

Hydroquinone: Vanadate oxidizes hydroquinone quantitatively in the presence of oxalic acid as catalyst.[31] The concentration of hydroquinone should be less than 0.01*M* and the acid concentration above 1*M*. The results agree with those obtained when ceric sulfate is used as titrant. However, the latter cannot be used in the presence of phenol or *o*-, *m*-, and *p*-cresols because of their oxidation to colored insoluble precipitates; sodium vanadate is without effect on these compounds. Resorcinol interferes owing to an induced oxidation.

Organic Acids: The use of oxalate for the standardization of vanadate solutions has already been considered (p. 634). Obviously the procedure may be applied to the determination of oxalate.[32] Tartaric acid may also be determined.[31] Morette and Gaudefroy[33] found that acyclic acids are not oxidized except where long side chains or double bonds are present. Formic acid is only slowly oxidized at high temperatures.

Indigo: Sodium vanadate is said to be a better titrant than permanganate for the determination of indigo. Oxalic acid is used as catalyst.[34]

Iodine Monochloride Method: Singh and Singh[35] used vanadate as titrant in a strong hydrochloric acid medium (7.0–7.5*N*) in the presence of iodine monochloride. The reaction is similar to that in the Andrews titration (p. 451; cf. p. 642). The same range of substances may be determined, e.g., iodide, arsenite, thiosulfate, ferrous, hydrazine. Similar indirect determinations of hydrogen peroxide, lead dioxide, copper, etc., are also possible.[36]

Procedure: To 25 ml. of the solution containing the test substance, add 30 ml. of concentrated hydrochloric acid, 5 ml. of 0.02*M* iodine monochloirde, and 5 ml. of chloroform. Cool to room temperature and titrate with the vanadate solution until the solution becomes pale green and the chloroform layer acquires a purple color. Shake the container and continue the dropwise addition of titrant until the purple color disappears from the organic solvent.

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[26] G. Gaudefroy, *Bull. soc. chim. France*, **1954**, 1222.

[27] M. N. Sastri, V. B. Rao, and G. G. Rao, *Current Sci. (India)*, 19, 90 (1950); cf. K. A. Hofmann and F. Küspert, *Ber.*, **31**, 64 (1898); W. C. Bray and E. J. Cuy, *J. Am. Chem. Soc.*, 46, 859 (1924).

[28] V. S. Syrokomskii, *Compt. rend. acad. sci. U.R.S.S.*, 46, 280 (1945).

[29] V. S. Syrokomskii and S. M. Gubel'bank, *Zhur. Anal. Khim.*, 6, 207 (1951).

[30] *Idem, ibid.*, 4, 203 (1949).

[31] G. G. Rao, V. P. Rao, and M. N. Sastri, *Current Sci. (India)*, **18**, 381 (1949).

[32] Cf. G. G. Rao and H. S. Gowda, *Current Sci. (India)*, 21, 188 (1952).

[33] A. Morette and G. Gaudefroy, *Compt. rend.*, **237**, 1523 (1953).

[34] G. G. Rao and M. N. Sastri, *Current Sci. (India)*, 21, 189 (1952).

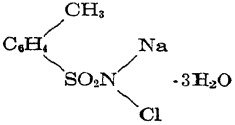
[35] B. Singh and R. Singh, *Anal. Chim. Acta*, **10**, 408 (1954).

[36] B. Singh and R. Singh, *Anal. Chim. Acta*, **11**, 412 (1954); **13**, 405 (1955).

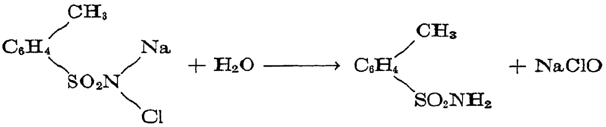
Note: The normality at the end-point should be 7.0–7.5*N* and more acid should be added, if necessary, to maintain this concentration.

CHLORAMINE

Chloramine T: Noll[37] was the first to propose the use of chloramine T as an oxidizing titrant. The compound is the sodium salt of *p*-toluenesulfochloramide; it has the formula



and behaves like a solution of hypochlorite in many of its reactions:[38]



It has the advantage that it may be used in alkaline or acid solution, and is said to be more stable than hypochlorite.

Preparation of 0.1*N* Chloramine T: Dissolve 15 g. of the commercial product in water and dilute to 1 liter.

Standardization. *Method 1:* To 25 ml. of 0.1*N* arsenite solution, add 0.5 g. of potassium iodide and 1 ml. of starch solution and titrate with the chloramine solution to a blue color.[37,39]

Method 2: Add 25 ml. of 0.5*N* potassium iodide and 25 ml. of 1:4 hydrochloric acid to 30 ml. of 0.1*N* chloramine T solution and titrate with 0.1*N* thiosulfate.[40]

Stability: There is some contradiction concerning the stability of solutions.[40,41] However, Poethke and Wolf[42] found that with high purity reagent the titer remained constant for 3 months when the solution was stored in a brown glass bottle.

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[37] A. Noll, *Chem. Ztg.*, **48**, 845 (1924); **64**, 308 (1940).

[38] Cf. R. Dietzel and K. Taufel, *Apoth. Ztg.*, **44**, 989, 1007 (1929).

[39] Cf. G. Charlot, *Bull. soc. chim. France*, **1941**, 226.

[40] K. Böttger and W. Böttger, *Z. anal. Chem.*, **70**, 225 (1927).

[41] O. Tomíček and B. Sucharda, *Collection Czech Chem. Communs.*, **4**, 285 (1932). (A bibliography of early uses of chloramine is given in this paper.)

[42] W. Poethke and F. Wolf, *Z. anorg. Chem.*, **268**, 244 (1952); cf. A. S. Komarowsky, W. F. Filonowa, and I. M. Korenman, *Z. anal. Chem.*, **96**, 321 (1934).

Methods for Determination of Compounds. *Arsenic and Antimony:* Trivalent arsenic and antimony may be determined by the procedure used for standardizing the solution of chloramine T. Other methods have been described. Tomíček and Sucharda[41, 43] titrated directly with chloramine T at 30–40°C. in a solution $1N$ in hydrochloric acid, methyl red being used as indicator. Poethke and Wolf[42] used *p*-ethoxychrysoidine or brilliant carmoisine as indicator in 5–7 per cent hydrochloric acid medium. In neutral or alkaline solution or at high acidities no indicator change took place; the indicator blanks varied with the acidity. Neither of these methods appears to have any advantage over the original.

Tin: The titration of tin(II) with chloramine T must be done in an inert atmosphere; a current of carbon dioxide is maintained above the surface of the liquid. The acidity should not exceed 3–5 per cent in hydrochloric acid. Rupp[44] used coarse zinc for the reduction; Mitchell and Ward[45] found lead to be superior (cf. p. 321).

Procedure:[45] Place 1 g. of sodium bicarbonate and a few milliliters of water in a large conical flask fitted with inlet and outlet tubes for the passage of carbon dioxide. Add concentrated hydrochloric acid to give a total amount of 40 ml., water to make the final volume 150 ml., and 2–3 pieces of lead foil (a surface area of about 24 sq. in.). Run in the solution containing 0.1–0.2 g. of tin, boil for $1^1/_2$ hours in a current of carbon dioxide, and then cool. Dissolve 15 g. of sodium hydroxide and a trace of sodium carbonate in air-free water, add to the cool solution, and dilute to about 250 ml. If necessary cool again, add a crystal of potassium iodide and some milliliters of starch solution and titrate with $0.1N$ chloramine T solution. One milliliter of $0.1N$ chloramine T corresponds to 5.935 mg. of tin.

Note: The cooling, dilution, and neutralization of the solution prevent further reduction by the metal.

[43] Cf. E. Rupp, G. Siebler, and W. Brachmann, *Pharm. Zentralhalle,* **66,** 33 (1925).

[44] E. Rupp, *Z. anal. Chem.,* **73,** 51 (1928).

[45] A. D. Mitchell and A. M. Ward, *Modern Methods in Quantitative Chemical Analysis,* Longmans Green, London, 1932, p. 150.

Other Metals: Iron (II),[41,42,46] mercury(I),[47] and thallium (I)[48] may be determined by titration with chloramine T. In the last determination variations of the Lang and the Andrews procedure with chloramine T as titrant were also successfully applied.

Ferrocyanide: Komarowsky *et al.*[49] studied the oxidation of several compounds with chloramine T. Ferrocyanide is rapidly oxidized at moderate temperatures in slightly acid solutions.

Procedure: To 10 ml. of the ferrocyanide solution add 5 ml. of 0.5*N* hydrochloric acid and an excess of 0.1*N* chloramine T. Heat to 40°C. Add 0.5–1 g. of sodium bicarbonate and an excess of standard arsenious trioxide solution. Add some crystals of potassium iodide and some starch solution and titrate with 0.1*N* chloramine T solution.

It is possible to work at room temperature if the mixture is allowed to stand for 1 hour before the neutralization and back-titration. Back-titration with thiosulfate is impossible because ferricyanide reacts with hydriodic acid.

Note: Poethke and Wolf[42] describe a similar procedure with brilliant carmoisine as indicator.

Hydrazine:[49] Hydrazine in bicarbonate solution can be directly titrated with chloramine solution. In acetate or neutral solution, it is necessary to add an excess and to back-titrate after for some time.

Procedure: To 25 ml. of solution add 0.5 g. of sodium bicarbonate, a crystal of potassium iodide, and some starch solution. Titrate slowly with chloramine to a blue color.

Hypophosphite:[49] To 20 ml. of the hypophosphite solution add 10 ml. of 1:5 sulfuric acid and 30 ml. of 0.1*N* chloramine solution. After 24 hours, add 2 g. of potassium iodide and titrate with thiosulfate.

The hypophosphite is oxidized to phosphite. Komarowsky *et al.* obtained slightly low results.

Nitrite: Several determinations with chloramine T were described by Van Eck;[50] the most interesting of these is the determination of nitrite.

Procedure:[45] To a suitable volume of the nitrite solution add a measured excess of chloramine T solution and a few milliliters of dilute acetic acid. The sodium salt is decomposed with the separation of free chloramine as a white cloud which rapidly decreases in intensity. After 2 minutes add an excess of 10 per cent potassium iodide solution and titrate the liberated iodine.

Run a blank on the amount of chloramine T used initially. The difference in titers represents the nitrite present. One milliliter of 0.1*N* thiosulfate corresponds to 2.30 mg. of nitrite.

Sulfite:[50] To 10 ml. of the sulfite or sulfurous acid solution add 50 ml.

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[46] B. N. Afanas'ev and A. V. Ural'skaya, *Zavskaya Lab.*, 15, 407 (1949).

[47] F. v. Bruchhausen and E. Hanzlik, *Apoth. Ztg.*, 40, 1115 (1925).

[48] A. J. Berry, *Analyst*, 59, 736 (1934).

[49] A. S. Komarowsky, W. F. Filonowa, and I. M. Korenman, *Z. anal. Chem.*, 96, 321 (1934).

[50] P. N. Van Eck, *Pharm. Weekblad*, 63, 1117 (1926).

of 0.1*N* chloramine T. Add 10 ml. of 10 per cent potassium iodide solution and titrate with thiosulfate.

Note: (1) Murthy[51] determined sulfite, sulfide, and thiosulfate in admixture by a combination of iodometric and chloramine T titrations.

Iodine Monochloride Methods: Several procedures have been described recently in which chloramine-T is used as a titrant in a strong hydrochloric acid medium in the presence of iodine monochloride. The end-point is detected as in the Andrews titration (p. 451) by the use of chloroform or carbon tetrachloride.[52]

The following substances may be determined in this way: iodide, hydrazine, iron(II), arsenic(III), antimony(III), tin(II), mercury(I), and thiocyanate.

Procedure: Transfer the compound to an Erlenmeyer flask fitted with a ground-in stopper and dissolve in 50 ml. of 1:1 hydrochloric acid. Add 5 ml. of 0.02*M* iodine monochloride and 5 ml. of chloroform. Titrate with chloramine T until the iodine color becomes straw yellow, stopper the flask, and shake. Continue the titration in this way until the chloroform layer changes from purple to very pale yellow.

Note: Several indirect determinations are also possible by reacting with an excess of a suitable standard reagent, e.g., potassium iodide or arsenious oxide, and back-titrating with chloramine T (cf. p. 465).[53]

Aldehydes: Formaldehyde and benzaldehyde may be determined as follows:[54]

Procedure: To 0.1–0.2 g. of aldehyde add 4–5 ml. of 10 per cent potassium iodide and 50 ml. of 0.1*N* chloramine-T and make alkaline with caustic soda. After 30 minutes acidify with hydrochloric acid and titrate with thiosulfate.

Notes: (1) Bionda[55] determined 2-furaldehyde by a similar method but he allowed the reaction to proceed for 90 minutes.

(2) Aldose sugars may be determined by titration with chloramine T.[56] The method appears to be less satisfactory than the conventional methods.

Ascorbic Acid: Leonhardt and Moeser[57] preferred to determine ascorbic acid with chloramine T rather than by the iodometric titration, which they found to be sluggish at the end-point, or the cerimetric titration, which gave high results. The reaction is said to be considerably faster than with the direct iodine titration.

[51] A. R. V. Murthy, *Current Sci. (India)*, 22, 342 (1953).

[52] B. Singh and K. C. Sood, *Anal. Chem. Acta*, 13, 301 (1955); cf. G. Jónás, *Magyar Gyógyszerésztud. Társasság Értesitöje*, 10, 526 (1934); *Chem. Abstr.*, 29, 1745 (1935).

[53] B. Singh and K. C. Sood, *Anal. Chim. Acta*, 13, 305 (1955).

[54] B. Carli and R. Airoldi, *Ann. chim. appl.*, 27, 56 (1937).

[55] G. Bionda, *ibid.*, 31, 31 (1941); cf. *Chem. Abstr.*, 49, 6032 (1955).

[56] C. L. Hinton and T. Macara, *Analyst*, 52, 668 (1927).

[57] H. Leonhardt and W. Moeser, *Z. anal. Chem.*, 122, 3 (1941).

Procedure: Dissolve 1 g. of ascorbic acid in water and dilute to 100 ml. Take a 10 ml. aliquot, add 40 ml. of water and 1 ml. of concentrated hydrochloric acid. Add potassium iodide and starch indicator and titrate with 0.1*N* chloramine T. One milliliter 0.1*N* chloramine T corresponds to 8.806 mg. of ascorbic acid.

Notes: (1) The accuracy is about 0.2 per cent.
(2) A few milligrams of potassium iodide is sufficient.

Other Organic Compounds: Organic sulfides have been determined by oxidation with chloramine T followed by iodometric titration of the excess.[58] Kinsey and Grant[59] determined mustard gas in this way; the method is empirical because the extent of the reaction depends on several factors.

Afanas'ev[60] determined several types of organic compound by titration with chloramine T; he used methyl red or indigo carmine as indicator. Satisfactory results were obtained for aldehydes, ketones (titration of excess bisulfite), glucose, glycerin, urea, thiourea, phenylhydrazine, and lactic acid.

Several other organic substances were determined by Singh *et al.*;[61] the titrations were done potentiometrically.

Chloramine B: Chloramine B has the formula $C_6H_5SO_2N(Na)$-$Cl{\cdot}3H_2O$ and was first proposed by Afanas'ev[62] as a substitute for chloramine T. Further investigations of the reagent have been carried out by Singh and his coworkers,[63] who have applied it to a wide range of determinations which are similar to the chloramine T methods. Bromination procedures were developed for various metals after precipitation as anthranilates[64] or oxinates.[65] This was accomplished by adding an excess of potassium bromide and chloramine B and then titrating the excess iodometrically. Various potentiometric titration methods have also been developed.[66]

This reagent is used exactly like chloramine T but appears to have no advantages. Hence it is unlikely to achieve even the limited use which chloramine T has attained.

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[58] J. W. Sease, T. S. Lee, G. Holzman, E. H. Swift, and C. Niemann, *Anal. Chem.*, **20**, 431 (1948).

[59] V. E. Kinsey and W. M. Grant, *Ind. Eng. Chem., Anal. Ed.*, **18**, 794 (1946).

[60] B. N. Afanas'ev, *Zavodskaya Lab.*, **15**, 1271 (1949); see also *Z. anal. Chem.*, **132**, 306 (1951).

[61] B. Singh, A. Singh, and M. Singh, *Research Bull. East Panjab Univ.*, **30**, 55 (1953).

[62] B. N. Afanas'ev, *Zavadskaya Lab.*, **16**, 1011 (1950).

[63] A. Singh, *Research Bull. East Panjab Univ.*, **43**, 17 (1954); B. Singh and K. C. Sood, *Anal. Chim. Acta*, **11**, 313, 317 (1954).

[64] A. Singh, *Research Bull. East Panjab Univ.*, **47**, 59 (1954).

[65] B. Singh, A. Singh, and S. R. Kapur, *ibid.*, **41**, 205 (1953).

[66] B. Singh and G. Singh, *Anal. Chim. Acta*, **10**, 81 (1954); **11**, 569 (1954).

SODIUM CHLORITE

This reagent was first suggested as an oxidizing titrant by Levi[67] and later by Jackson and Parsons.[68] It does not appear to possess any advantages over earlier reagents and has not achieved wide application.

Levi[67] suggested various analytical applications but details are lacking. Jackson and Parsons[68] determined sulfite (and bisulfite). The direct oxidation is too slow for practical purposes, but is accelerated by the addition of small amounts of iodide and the end-point is detected by the appearance of the blue starch-iodine color.

$$ClO_2^- + 4H^+ + 4e \longrightarrow Cl^- + 2H_2O$$

Arsenite is oxidized quantitatively by chlorite in a bicarbonate medium in the presence of osmic acid as catalyst.[69] If the titration is done slowly and very carefully the osmic acid also serves as indicator; no other suitable indicator has yet been found for the direct titration. The more satisfactory way to determine arsenite is to add a slight excess to a standard chlorite solution and to back-titrate with a solution of iodine; this method seems to have little to recommend it.

When the solution is standardized iodometrically the titration of the liberated iodine may be done forthwith if sulfuric or phosphoric acid is used for the acidification. With acetic acid the solution must be allowed to stand for 5 minutes.

Preparation and Standardization: Prepare a solution of $0.1N$ sodium chlorite by weighing out the appropriate amount and dissolving in water (2.261 g. per liter). Add an accurately measured amount of this solution to a stoppered conical flask containing 75 ml. of distilled water, 15 ml. of 10 per cent potassium iodide solution, and 15 ml. of 30 per cent acetic acid. Stopper the flask, and leave in the dark for 5 minutes. Titrate the liberated iodine with standard sodium thiosulfate solution, using 5 ml. of 1 per cent starch indicator near the end-point.

Store the chlorite solution in a black-painted bottle to exclude light. In these conditions the solution is stable for several months.

Determination of Sulfite:[68] Transfer the sulfite solution to a conical flask containing 100 ml. of distilled water, 15 ml. of 10 per cent potassium iodide solution, 15 ml. of 30 per cent acetic acid, and 5 ml. of 1 per cent starch solution. Titrate rapidly with the sodium chlorite until near the end-point, and then dropwise until the blue color persists. It is preferable to avoid shaking the solution until most of the sodium chlorite has been added.

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[67] G. R. Levi, *Atti accad. Lincei*, **31**, I, 370 (1922); *Gazz. chim. ital.*, **52**, 58 (1922); **53**, 105 (1923). G. R. Levi, *Ind Eng. Chem., Anal. Ed.*, **9**, 250 (1937).

[68] D. T. Jackson and J. L. Parsons, *Ind. Eng. Chem., Anal. Ed.*, **9**, 14 (1937).

[69] E. G. Brown, *Anal. Chim. Acta*, **7**, 494 (1952).

One milliliter of 0.1N chlorite corresponds to 4.003 mg. of sulfite.

Note: Solutions of sulfite containing lignin derivatives, sugars, and other organic matter can be titrated without interference.

Determination of Iodide: Yntema and Fleming[70] used a standard solution of chlorite for the determination of iodide. At a pH of about 5 the following reaction occurs:

$$3ClO_2^- + 2I^- \longrightarrow 2IO_3^- + 3Cl^-$$

The best procedure is to add a small excess of chlorite and back-titrate with a standard iodide solution.

Procedure: To the solution containing 0.04–0.07 g. of iodide, add 1 ml. of 2M acetic acid, 9 ml. of 2M sodium acetate, and some starch solution. Titrate with 0.1N or 0.2N sodium chlorite until the discharge of the blue color indicates that all the iodine first formed by the oxidation of the iodide has been converted to iodate. Add a small excess of chlorite and back-titrate with 0.02M potassium iodide to a permanent amber color.

Each milliliter of 0.2N chlorite is equivalent to 4.231 mg. of iodide.

Notes: (1) The direct titration gave inconsistent results.

(2) For a description of the properties of sodium chlorite (anhydrous or trihydrate) see M. C. Taylor, J. F. White, G. P. Vincent, and G. L. Cunningham, *Ind. Eng. Chem.*, 32, 899 (1940).

POTASSIUM FERRICYANIDE

The oxidation potential of the ferri-ferrocyanide system is the same in neutral or alkaline solution, the normal potential being of the order of +0.45 v.[71] Ferricyanide in alkaline medium finds wide application in the determination of reducing sugars (p. 345). The compound is obtainable in a high state of purity and serves as its own primary standard.

Determination of Sulfide: In alkaline medium, sulfide is oxidized by ferricyanide to sulfur if the pH is properly adjusted; if the pH is incorrect, further oxidation to sulfate may occur. Charlot[72] found that in an ammonium chloride-ammonia buffer of pH 9.4, the reaction goes quantitatively to sulfur:

$$S^{2-} + 2Fe(CN)_6^{3-} \longrightarrow S + 2Fe(CN)_6^{4-}$$

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[70] L. F. Yntema and T. Fleming, *Ind. Eng. Chem., Anal. Ed.*, 11, 375 (1939). cf. S. Škramovský, Z. Tauer, and J. Novotný, *Chem. Listy*, 48, 1335 (1954).

[71] Cf. H. H. Willard and G. D. Manalo, *Ind. Eng Chem., Anal. Ed.*, 19, 462 (1947).

[72] G. Charlot, *Bull. soc. chim. France*, (5) 6, 1447 (1939).

Ferrous dimethylglyoxime, which changes from red to colorless at the endpoint, is used as reversible indicator.

Indicator: Mix in a test tube 1 ml. of 0.02N ferrous sulfate, 4–5 ml. of a saturated alcoholic solution of dimethylglyoxime, and 0.5 ml. of concentrated ammonia. The solution is slowly oxidized by air.

Buffer Solution: Mix 70 ml. of concentrated ammonia and 50 g. of ammonium chloride and dilute to 1 liter with water.

Procedure: Transfer 20 ml. of the buffer solution to an Erlenmeyer flask and add a few drops of indicator solution to give a pink color. Remove the air by passing hydrogen for 5 minutes. Add a measured volume of the sulfide solution and titrate immediately with standard ferricyanide solution until the pink color has disappeared and does not return.

Notes: (1) Oxygen interferes and must be removed. Sulfite interferes but can be removed by precipitation with an excess of barium chloride; after the addition of the precipitant, the mixture is set aside for 10 minutes before titration.

(2) Charlot[73] also titrated hydrosulfite with ferricyanide:

$$S_2O_4^{2-} + 2Fe(CN)_6^{3-} + 4OH^- \longrightarrow 2SO_3^{2-} + 2Fe(CN)^{4-} + 2H_2O$$

Procedure: Add to an Erlenmeyer flask 1 drop of 0.02N ferric chloride solution, 4–5 drops of a saturated dimethylglyoxime solution in alcohol, 100 ml. of water, 7 ml. of concentrated ammonia, and 5 g. of ammonium chloride. Remove the air with nitrogen, add the hydrosulfite solution, and titrate with 0.02N or 0.1N ferricyanide solution until the color changes sharply from red to pale yellow.

(3) Willard and Manalo[74] described the determination of several substances by oxidizing with excess of ferricyanide and back-titrating with standard vanadyl sulfate in alkaline solution. The methods appear to be of little practical significance; the original paper should be consulted for details.

FERRIC SALTS

Thiosulfate: Jellinek and Winogradoff[75] have suggested methods in which ferric chloride is used as a substitute for iodine; the procedures are based on the oxidation of thiosulfate to tetrathionate by ferric chloride.

$$2S_2O_3^{2-} + 2Fe^{3+} \longrightarrow 2Fe^{2+} + S_4O_6^{2-}$$

The ferric solution is titrated at about 50° C. with thiosulfate; a mixture of methylene blue and fuchsin is used as indicator. With excess of thiosulfate, methylene blue is bleached to the colorless leuco base.

Kolthoff and Tomíček[76] examined this method but were never able to achieve an accuracy of better than 1 per cent even under the optimum conditions. Slightly better results were achieved with meconic acid as indicator.

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[73] G. Charlot, *Bull. soc. chim. France*, (5) 6, 977 (1939).

[74] H. H. Willard and G. D. Manalo, *Ind. Eng. Chem., Anal. Ed.*, 19, 167 (1947).

[75] K. Jellinek and L. Winogradoff, *Z. anorg. Chem.*, 129, 15 (1925).

[76] I. M. Kolthoff and O. Tomíček, *Pharm. Weekblad*, 61, 1205 (1924).

This acid yields a red ferrimeconate with ferric iron and the red color disappears when all the ferric iron has been reduced. Copper catalyzes the reaction of iron(III) and thiosulfate; in the presence of too much copper, however, the end-point is unsatisfactory. For general purposes the procedure is not to be recommended.

Procedure: To about 100 ml. of the ferric solution containing less than 3 ml. of $4N$ hydrochloric acid add 1 drop of $0.5N$ copper sulfate solution and heat to 60°C. Titrate with $0.1N$ thiosulfate, adding 1 ml. at a time and waiting until the violet brown color of the ferrithiosulfate has disappeared. Titrate in this way until no violet color appears when thiosulfate is added. Add 1–2 ml. of 0.6 per cent aqueous meconic acid solution and heat to boiling. Continue the titration, boiling after each added drop of titrant, until the red color completely disappears.

Note: Near the end-point, the reaction is very slow. The titration is troublesome to carry out and must be done very slowly. The accuracy is at best 0.5 per cent.

Titanium: Trivalent titanium is often titrated with a standard solution of ferric alum in the presence of thiocyanate as indicator (cf. p. 613). Various methods of reduction of titanium(IV) have been used.[77] Bischoff[77] reduces titanium (IV) with pure iron dust in an atmosphere of carbon dioxide and then titrates in this way (ammonium sulfate is added because it helps to stabilize the titanous solution; cf. p. 155).

Procedure: Dissolve 0.2 g. of titanium dioxide and 4 g. of ammonium sulfate in 10 ml. of concentrated sulfuric acid. Cool, dilute with 100 ml. of 1:5 sulfuric acid, and shake well. Pass carbon dioxide through a 750 ml. Erlenmeyer flask until it is air-free and add 4–5 g. of pure iron. Pass a strong stream of carbon dioxide through the flask for 10 minutes and then add the titanium solution followed by 20 ml. of 1:1 sulfuric acid. When the evolution of hydrogen ceases, after 5–10 minutes of frequent shaking, heat to gentle boiling, swirl, and boil until all the solid material has dissolved. Then boil for 5 minutes, cool in water under the carbon dioxide atmosphere, and titrate with $0.1N$ ferric sulfate solution (Note 1) after adding 10 ml. of 5 per cent potassium thiocyanate. A permanent reddish color indicates the end-point.

Notes: (1) The $0.1N$ ferric sulfate is prepared by dissolving 5.585 g. of pure iron in excess hydrochloric acid and oxidizing with nitric acid. After evaporation on a bath, 30 ml. of concentrated sulfuric acid is added and the mixture is boiled until heavy fumes appear. Cool the solution, dilute with water, and boil out any nitrogen oxides. Dilute to 500 ml. and boil until the solution is clear. If necessary, filter and dilute to the mark in a 1 liter flask. Standardize in the usual way with permanganate. A standard solution of ferric alum could probably be used [Authors].

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[77] Cf. C. Winterstein, *Z. anal. Chem.*, **117**, 81 (1938); **119**, 385 (1940); A. Claassen and J. Visser, *Rec. trav. chim.*, **60**, 213 (1941); F. Bischoff, *Z. anal Chem.*, **130**, 195 (1950); P. Wehber and H. Hahn, *ibid.*, **136**, 325 (1952).

(2) Titanium may be determined in the presence of columbium and tantalum by reduction with zinc amalgam in the presence of an excess of tartaric acid (greater than 25 per cent). Only titanium is reduced under these conditions.[78]

Tin: Schlüttig[79] has developed a direct titration of stannous tin with ferric chloride, using indigo carmine as indicator. In strong hydrochloric

$$Sn^{2+} + 2Fe^{3+} \longrightarrow Sn^{4+} + 2Fe^{2+}$$

acid solution (about $5N$) the color change of indigo carmine from soft yellow to indigo blue is very sharp; the approach of the end-point is signaled by a bottle-green color. It is necessary to provide an atmosphere of carbon dioxide because of the sensitivity of the stannous tin to air-oxidation. The original paper should be consulted for details.

Uranium: An elevated temperature must be used when quadrivalent uranium is titrated with a ferric salt, owing to the sluggish nature of the reaction.[80] When thiocyanate is used as indicator the temperature must be maintained below 90°C. to avoid decomposition of the ferrithiocyanate complex. This procedure is less accurate than that using a potentiometric end-point; hence the latter is to be preferred. It is necessary to exclude air completely in both processes to obtain the most accurate results. The original paper should be consulted for details.

MANGANIC SALTS

Manganic sulfate was first suggested as an oxidimetric reagent by Ubbelohde.[81] It has some advantages over potassium permanganate, for ferrous salts may be determined in the presence of chlorides (cf. p. 77), oxalates may be titrated at much lower temperatures, and nitrites, hydrogen peroxide, and vanadium(II) are much more smoothly oxidized. Ubbelohde considered that this efficiency was due to the fact that only a simple valency change occurred:

$$Fe^{2+} + Mn^{3+} \longrightarrow Fe^{3+} + Mn^{2+}$$

The solution has a deep red tint and serves as its own indicator. Unfortunately, in our experience, the reagent is unstable and deteriorates rapidly. Furthermore, when prepared by Ubbelohde's method (oxidation of manganous sulfate with permanganate at high acid concentration) much manganese dioxide precipitates. After this has been removed by filtration, the resulting solution is too weak to be used for most purposes. In any case it is only possible to prepare small amounts of solution because of the difficulty of keeping the mixture cool during the acidification.

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[78] O. Tomíček, K. Spurný, L. Jerman, and V. Holeček, *Collection Czech Chem. Communs*, 18, 757 (1953).

[79] W. Schlüttig, *Z. anal. Chem.*, 70, 55 (1927); cf. K. Jellinek and L. Winogradoff, *Z. anorg. Chem.*, 129, 15 (1923).

[80] *Analytical Chemistry of the Manhattan Project*, C. J. Rodden, ed., McGraw-Hill, New York, 1950, p. 70.

[81] A. R. J. P. Ubbelohde, *J. Chem. Soc.*, 1935, 1505.

Belcher and Townend[82] prepared several double salts of manganese(III) in the expectation of finding a more stable reagent. Potassium manganic sulfate was more stable than the single salt but not sufficiently so for it to be recommended as a titrant. Belcher and West[83] prepared a stable titrant by forming the pyrophosphato complex. They first prepared the solution by oxidizing manganous sulfate with permanganate or bismuthate, but later by dissolving manganic phosphate in sodium pyrophosphate.

This reagent was stable over a period of 6 weeks, but its tinctorial properties were less than those of manganic sulfate and it was necessary to use an indicator to observe the end-points obtained. Several determinations were possible, and ferrous iron could be readily titrated even in 5*N* hydrochloric acid. It was concluded that manganic pyrophosphate, although more stable than manganic sulfate, was a much weaker oxidant. The result of stabilizing the manganic ion against decomposition was to stabilize it to some extent against reduction. This was confirmed by determining the redox potentials of manganic sulfate and pyrophosphate; the latter was 0.18 v. lower under the experimental conditions used.

Belcher and West[83] concluded that although it is possible to stabilize the manganic ion, it is doubtful if the reagent has any practical value, for the stability is less than that of potassium dichromate or ceric sulfate, which can also be used for the titration of ferrous iron in the presence of hydrochloric acid. Nevertheless the reagent appears to have found some limited use.[84]

In view of the observations of Belcher and West, details of the use of the reagent will not be given here; they should be sought in the original literature.

HYDROGEN PEROXIDE

Hydrogen peroxide was used as a titrant by Job[85] to determine cerium(IV). Jellinek and Krebs[86] titrated iron(II) and tin(II) with a solution of hydrogen peroxide and used a titanium(IV) solution as indicator. In a later paper,[87] starch-iodide or ferric thiocyanate was preferred as indicator in the stannous titration. Other determinations were tried with little success.

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[82] R. Belcher and J. Townend, unpublished studies.

[83] R. Belcher and T. S. West, *Anal. Chim. Acta*, **6**, 322 (1952); cf. I. M. Kolthoff and J. L. Watters, *Ind. Eng. Chem., Anal. Ed.*, **15**, 8 (1943).

[84] T. Ikegami, *J. Chem. Soc. Japan*, **52**, 173 (1949); N. Sato, *ibid.*, **55**, 59 (1952).

[85] A. Job, *Compt. rend.*, **128**, 101 (1899).

[86] K. Jellinek and P. Krebs, *Z. anorg. Chem.*, **130**, 276 (1923).

[87] K. Jellinek and W. Kühn, *Z. anorg. Chem.*, **138**, 84 (1924).

Erdey and Buzás[88] titrated ferricyanide, arsenite, and hypohalites in hot alkaline solution with hydrogen peroxide stabilized with 8-hydroxyquinoline. This solution is said to be stable for 2 months One milliliter of 0.5 per cent lucigenin (dimethyldiacridilium nitrate) was used as chemiluminescent indicator.

An interesting modification of the titrant has been described by Beck.[89] He stabilizes the solution with titanium(IV), and the intensely orange-colored solution serves as its own indicator. The solution is stable for 14 days; boiling for 1 hour or exposure to ultraviolet radiation causes no measurable change.

The reagent has so far only been applied to the determination of cerium(IV).

$$2Ce^{4+} + H_2O_2 \longrightarrow 2Ce^{3+} + 2H^+ + O_2$$

Preparation and Standardization of 0.1*N* Solution: To 500 ml. of twice distilled water add 5.65 g. of 30 per cent hydrogen peroxide, and 110 ml. of *M* titanic sulfate. Dilute to 1000 ml. with twice distilled water. Standardize iodometrically (p. 283).

Determination of Cerium: To the solution containing 50–350 mg. of cerium(IV) add 20 ml. of 20 per cent sulfuric acid, heat to 50°C., and titrate till a yellow color appears.

Notes: (1) It is necessary to maintain a high acidity to prevent the hydrolysis of titanium(IV) and cerium(IV) salts.

(2) Cations of the third column of the periodic table which usually accompany cerium do not interfere with the titration. Of course, other strong oxidizing agents, such as permanganate, interfere [Authors].

POTASSIUM PERIODATE

The use of potassium periodate as a precipitant for various metals with subsequent iodometric determination of the precipitate has already been considered (p. 274). The further important uses of the reagent for the oxidation of certain organic compounds (the Malaprade reaction) have also been described (Chapter XI, p. 475). Some limited use has also been made of potassium periodate for the direct titration of various reducing agents.

Syrokomskii and his coworkers[90] titrated tellurite, iron, antimony, and arsenic in this way, diphenylamine or *N*-phenylanthranilic acid being used as indicator. Mázor and Erdey[91] titrated vanadium(II); starch, *p*-ethoxychrysoidine, saphranin T, and neutral red were all suitable as indicators. These investigators also used a potentiometric method.

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[88] L. Erdey and I. Buzás, *Acta Chim. Acad. Sci. Hung.*, 6, 77 (1955).

[89] M. T. Beck, *Acta Chim. Acad. Sci. Hung.*, 5, 209 (1955).

[90] V. S. Syrokomskii and R. N. Knyazeva, *Zavodskaya Lab.*, 16, 1041 (1950); V. S. Syrokomskii and S. I. Melamed, *ibid.*, 16, 131, 273 (1950).

Singh and his coworkers[92] have used this reagent under the conditions of the Andrews and the Lang titrations. The same range of direct and indirect determinations is possible (pp. 457–472).

The use of potassium periodate for the direct titration of inorganic substances appears to have no advantage over well-established titrants, and the reagent is more expensive than potassium iodate; methods involving its use appear to be only of academic interest.

POTASSIUM PERIODATOPERCUPRATE

It has been known for many years that copper can form certain complex compounds in which it has a valency higher than is normally associated with the simple ions. The history up to 1925 of compounds containing tervalent copper has been reviewed by Votis.[93] Malaprade[94] succeeded in isolating the sparingly soluble sodium diperiodatocuprate, $Na_7(Cu(IO_6)_2)$. From the work of Votis and Malaprade and from further work of Malatesta[95] it may be concluded that copper may be oxidized from the bivalent to the tervalent state by means of persulfate, but that the tervalent ion is unstable, and requires to be stabilized by coordination with a suitable anion. This stabilizing function may be performed by periodate or tellurate, the former being particularly suitable because of its greater stability and ease of preparation.

Keyworth and Stone[96] examined the reagent in solutions which were ca. $0.05M$ but concluded that it was not satisfactory at millimole levels. The complexing ion participated in the oxidation and the detection of endpoints gave trouble.

A number of interesting determinations are said to be possible with the percuprate reagent. It is recommended by the authors that the methods given briefly below be checked before the results are accepted. The excess of persulfate can be a source of error.

Preparation of $0.01M$ Reagent:[97] Boil 0.23 g. of potassium periodate,

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[91] L. Mázor and L. Erdey, *Acta Chim. Acad. Sci. Hung.*, **2**, 331 (1952).

[92] B. Singh and A. Singh, *J. Indian Chem. Soc.*, **29**, 34, 517 (1952); **30**, 143 (1953); *Anal. Chim. Acta*, **9**, 22 (1953).

[93] M. Votis, *Rec. trav. chim.*, **44**, 425 (1925).

[94] L. Malaprade, *Compt. rend.*, **204**, 979 (1937).

[95] L. Malatesta, *Gazz. chim. ital.*, **71**, 467, 580 (1941).

[96] D. A. Keyworth and K. G. Stone, *Anal. Chem.*, **27**, 833 (1955).

[97] G. Beck, *Mikrochemie*, **35**, 169 (1950).

0.125 g. of copper sulfate pentahydrate, 0.14 g. of potassium persulfate, and 0.8 g. of potassium hydroxide with 30 ml. of water until a clear brown solution is obtained. Cool and dilute to 50 ml.

Notes: (1) Potassium salts must be used throughout; sodium salts yield a precipitate of sodium diperiodatocuprate. Potassium iodate may be used instead of periodate provided that an appropriately larger amount of persulfate is used.
(2) Similarly, in the preparation of the tellurate compound, the more readily available tellurium dioxide or potassium tellurite may be used instead of potassium tellurate. These substances are dissolved in potassium hydroxide, and after addition of copper sulfate the mixture is oxidized with persulfate to give ditelluratocuprate, $K_5H_4(Cu(TeO_6)_2)$.[95]
(3) These solutions are stable for several days.

Standardization:[97] The reagent may be standardized against glucose solution. One molecule of glucose reacts with eight atoms of copper.

Procedure: Take an aliquot of 0.2–0.3 ml. of 0.1 per cent glucose solution and add 30 ml. of water and 3 pellets of pure potassium hydroxide. Titrate from a microburette to a green color which is stable for 1 minute. The titration can be carried out in the cold and atmospheric oxygen does not interfere.

Determination of Calcium: The use of naphthalhydroxamate for the gravimetric or colorimetric determination of calcium has been described by Beck[98] and contains no unusual features, but the adaptation of the method to a titrimetric procedure presented a considerable amount of difficulty. Direct titration of the calcium naphthalhydroxamate with permanganate, dichromate, iodine, or ferric salts failed to give good results. The substance is slowly oxidized by sodium hypochlorite, but the final iodometric titrations were inconsistent. The only successful oxidant was potassium diperiodatocuprate in alkaline solution. The oxidation with this reagent takes place in two stages: the first, involving 4 atoms of copper per molecule of calcium naphthalhydroxamate, takes place quite rapidly and results in conversion to naphthalic acid and nitrite ions; the second stage takes place very slowly, involves 2 atoms of copper, and results in the oxidation of nitrite to nitrate. The latter reaction takes place more rapidly at pH 6–7.

Procedure: Boil 1 ml. of an approximately $0.5N$ solution of calcium with sodium naphthalhydroxamate for a short time and then separate the precipitate by centrifuging. Wash successively with 20 per cent, 50 per cent, and pure acetone and suspend in 5 per cent potassium hydroxide. Titrate the warm solution with $0.01M$ potassium periodatocuprate solution. The end-point is very sharp and is marked by the appearance of a green color arising from the combination of the colors of bivalent and trivalent copper. It is detectable with an excess of 0.005 ml. of titrant corresponding to 0.1 μg. of calcium.

Other Determinations[98]*:* Several other inorganic substances have been determined by direct titration with potassium periodatocuprate. These include some of the common reducing agents, such as arsenious oxide, antimonious oxide, and sodium thiosulfate, and the sulfides of such elements as arsenic, antimony, phosphorus, molybdenum, tin, lead, and zinc in the form of alkaline solutions of the (higher) sulfides. The reaction suggested for the oxidation of thiosulfate is

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[98] G. Beck, *Mikrochemie*, **36/37**, 245 (1951).

$$S_2O_3^{2-} + 2OH^- + 4O \longrightarrow 2SO_4^{2-} + H_2O$$

while that for the titration of arsenic sulfide appears to be

$$As_2S_3 + 2O + 6OH^- \longrightarrow AsS_2O_2^{3-} + AsSO_3^{3-} + 3H_2O$$

In boiling solution, further oxidation takes place more slowly:

$$AsS_2O_2^{3-} + 4O + H_2O \longrightarrow AsSO_3^{3-} + H_2SO_4$$

Of greater significance is the titration of cyanides, the procedure affording a method for determining cyanides without interference from halides. The reaction appears to be

$$CN^- + 2OH^- + 5O \longrightarrow CO_3^{2-} + NO_3^- + H_2O$$

Chromic salts can be titrated with potassium diperiodatocuprate but, although the oxidation proceeds rapidly and smoothly, the end-point is difficult to detect owing to the intense yellow color of the chromate formed in the reaction. For this titration, therefore, potassium periodatonickelate is recommended in preference to the copper compound.

Procedure for Arsenic, Antimony, Thiosulfate, Sulfide, or Cyanide: Measure out 0.5 ml. of solution and add 5 ml. of 10 per cent potassium hydroxide solution. Titrate with the reagent to the green end-point, using a microburette. In the case of the cyanide a transient violet color appears at the beginning of the titration.

In addition to the determination of glucose as in the standardization method, the reagent may be employed for the titrimetric determination of other organic compounds, such as reducing sugars,[98] amino acids and proteins,[99] in biological fluids.

OTHER OXIDIZING TITRANTS

Various other oxidizing titrants have been recommended. They appear to have no advantage over conventional methods and generally seem to be more troublesome. The original papers should be consulted for details of their use. Potassium chlorate has been used for the titration of tin(II)[100] and vanadium(II);[101] iodine monochloride for the titration of tin(II), mercury(I), iron(II),[102,103] and various organic compounds.[102,104]

2. Reducing Titrants.

ARSENIOUS OXIDE

We have already seen in the discussion of standard substances in Chapter II (p. 41) that arsenious oxide can easily be obtained in a pure state. A standard solution can be prepared by dissolving a known amount of the pure material in sodium hydroxide and neutralizing the solution. Trivalent arsenic can be accurately titrated in bicarbonate solution with iodine or hypochlorite, and in hydrochloric acid solution with bromate or iodate. Various uses of arsenious solutions have already been considered if back-titration of the excess is involved. Direct titrations are also possible.

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[99] G. Beck, *Mikrochemie,* **38,** 1, 152 (1951); **39,** 147 (1952). *Mikrochim. Acta,* **1956,** 977.

[100] R. M. Kulwarskaja, *Z. anal. Chem.,* **89,** 199 (1932).

[101] L. Erdey and L. Mázor, *Acta Chim. Acad. Sci. Hung.,* **3,** 469 (1953).

[102] Y. A. Fialkov and F. E. Kagan, *Chem. Abstr.,* **47,** 12099 (1953).

[103] J. Čihalík, *Chem. Listy,* **49,** 1167 (1955).

[104] J. Čihalík and D. Vavrejnova, *ibid.,* **49,** 693, 1176 (1955).

Methods for Determination of Compounds. ***Hypochlorite:*** Calcium hypochlorite and other hypochlorites can be determined by the Penot method,[105] in which arsenious solution is added until, after thorough stirring, a drop of the solution does not give a blue color with iodide-starch paper. The method gives exact results and chlorate does not interfere. Kolthoff[106] recommended methyl red or methyl orange indicator.

Procedure: Triturate 10 g. of calcium hypochlorite with a little water in a porcelain mortar, adding a small excess of sodium hydroxide. Dilute to 1 liter with water in a volumetric flask, shake well, and filter. Use this solution in the burette. Pipette 25 ml. of $0.1N$ arsenious trioxide solution into a flask, add 5 ml. of $4N$ acetic acid, and 3 drops of 0.2 per cent methyl red and titrate the solution to colorless.

Note: Chlorate does not interfere but chlorite reacts slowly with arsenite and prevents the clear observation of the end-point.

Gay-Lussac[107] assayed hypochlorite by running it from a burette into a standard arsenite solution; indigo was used as indicator. This form of the titration has been followed by later workers, one of the latest modifications being due to Sinn,[108] who used quinoline yellow as reversible indicator and included bromide and acetate in the standard arsenite solution.

Procedure: Dilute the concentrated sodium hypochlorite solution with 50 or 100 times its volume of water or dissolve 7 g. of calcium hypochlorite in water and dilute to 1 liter. Place 10 ml. of $0.2N$ arsenious acid solution (Note 1) in a flask and add 2–3 drops of 0.2 per cent aqueous quinoline yellow solution. Titrate with the unknown hypochlorite solution; the indicator tends to discolor near the end-point, and the hypochlorite should then be added slowly. The end-point is sharp from greenish yellow to colorless.

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[105] Penot, *Bull. Soc. Ind. Mulhouse*, 1852, No. 118; cf. J. Clarens, *Compt. rend.*, 159, 183 (1914); A. Schleicher, *Z. anal. Chem.*, 62, 329 (1923); A. Lassieur and D. Jouslin, *Chim. anal.*, **33**, 45 (1951).

[106] I. M. Kolthoff, *Pharm. Weekblad*, **55**, 1289 (1918).

[107] J. L. Gay-Lussac, *Ann. chim. et phys.*, (2) 60, 225 (1835).

[108] V. Sinn, *Chim. anal.*, 29, 58 (1947).

Notes: (1) The arsenious acid solution is prepared by dissolving 19.782 g. of arsenious trioxide in 120 ml. of $2.5N$ sodium hydroxide and diluting to 1.5 liters. After the addition of 56 g. of sodium bromide dihydrate to give a $0.2N$ bromide solution, the mixture is neutralized with acetic acid to litmus paper and a volume of acetic acid equal to one tenth of that required for neutralization is added.

(2) Young and Das Gupta[109] could not obtain a color change when Sinn's procedure was applied, but satisfactory results were obtained by direct titration with arsenite. Belcher,[110] however, obtained excellent results with Sinn's procedure and criticized the conditions of Young and Das Gupta[109] which would allow rapid destruction of the indicator to take place before the end-point; cf. p. 577.

(3) Erdey and Buzás[111] titrate hypochlorite and hypobromite with standard arsenite in alkaline medium in the presence of luminol as a chemiluminescent indicator; cf. p. 581. The end-point of the hypochlorite titration is reversible.

Periodate: Gleu and Katthän[112] titrate periodate with $0.1N$ arsenic trioxide in dilute sulfuric acid medium with ferroin as indicator and a trace of ruthenium salt as a catalyst. The oxidation of ferroin by periodate in acid medium occurs slowly but is almost instantaneous in the presence of a trace of ruthenium salt. Osmium tetroxide is not suitable for the purpose, for its oxidation potential is not high enough; ruthenium tetroxide has the required oxidation potential.

When periodate is titrated with arsenic trioxide the reduction takes place first to iodate. As long as there is periodate present the indicator remains in the oxidized slightly bluish state, but the first excess of arsenic trioxide brings about the color change of the indicator to red ferroin.

Hydrazine sulfate can be used instead of arsenic trioxide.

Chromate and Vanadate: Arsenite solution can be used very suitably for the determination of chromate in presence of vanadate. In acid solution, the chromate is selectively reduced and the excess of arsenite can be back-titrated with permanganate.

Spitalsky[113] first described the determination of chromate with arsenite solution, but the method has been little used because so many other simple methods exist. Kolthoff and Sandell[114] have applied the method to the rapid analysis of chromium-vanadium steels.

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[109] J. H. Young and R. N. Das Gupta, *Analyst*, **74**, 367 (1949).

[110] R. Belcher, *Anal. Chim. Acta*, **5**, 27 (1951).

[111] L. Erdey and I. Buzás, *Acta Chim. Acad. Sci. Hung.*, **6**, 123 (1955).

[112] K. Gleu and W. Katthän, *Ber.*, **86**, 1077 (1953).

[113] E. Spitalsky, *Z. anorg. Chem.*, **69**, 179 (1911); cf. R. Lang, *ibid.*, **152**, 205 (1926); R. Lang and J. Zwerina, *Z. Elektrochem.*, **34**, 364 (1928); E. Zintl and P. Zaimis, *Z. angew. Chem.*, **40**, 1286 (1927); **41**, 543 (1928).

[114] I. M. Kolthoff and E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **2**, 140 (1930).

Procedure: To the vanadate-containing solution of chromate (less than 0.05–0.075 g. of chromium), which should be about 1–2N in sulfuric acid, add an excess of arsenite solution containing 10 g. of sodium chloride per liter. After 5 minutes (or longer) add 1–2 drops of 0.0025N potassium iodide solution as catalyst and titrate with permanganate to the color change from green to blue-green.

Notes: (1) The method is accurate even in the presence of large amounts of vanadate. If much iron is present, 5–10 ml. of 85 per cent phosphoric acid should be added to improve the end-point. If much manganese is present, the solution becomes brown after the addition of the arsenious oxide solution because of the formation of a complex manganic salt. A trace of iodide catalyzes the reduction of the manganic complex by arsenite. The color change can be detected with 1 drop of permanganate solution.

(2) Determination of vanadate after reduction of chromate: After the back-titration of excess arsenite, add some drops of arsenite solution to remove the excess of permanganate. Titrate the vanadate with ferrous sulfate, using diphenylbenzidine as indicator (p. 607).

(3) The method can be applied to the analysis of steel. Use 2–3 g. of steel for each per cent of chromium (e.g., take 4–6 g. of a steel containing about 2 per cent of chromium). Dissolve the sample by boiling with 25 ml. of water, 3–4 ml. of 85 per cent phosphoric acid, and concentrated sulfuric acid (1.5 ml. for each gram of sample). Oxidize the ferrous iron with nitric acid and boil out the nitrogen oxides. Dilute to 100 ml. and oxidize chromium and vanadium to their highest oxidation states with bromate (p. 633). Cool the solution, add 5–8 ml. of 85 per cent phosphoric acid, and 1–2 drops of 0.0025N potassium iodide and proceed as above.

Szabó and Csányi[115] prefer a catalyst mixture consisting of 0.021 g. of potassium iodide and 0.005 g. of manganese sulfate in 250 ml. of water; 5 ml. of this solution is used per determination.

Procedure: Acidify the sample with 5–6 ml. of concentrated sulfuric acid and dilute to 50–60 ml. with water. Cool, add 5 ml. of catalyst solution and 1 drop of 1 per cent diphenylamine indicator. Titrate with standard arsenite until the blue color turns light green. If the blue color returns within 5 minutes, add 1 more drop of titrant. The indicator correction is 0.05 ml. of 0.1N arsenite solution.

Notes: (1) Mercury and thiocyanate ions interfere.

(2) The method may be used for the determination of chromium in steel, but fluoride must be added to mask the iron (0.5 g. of ammonium fluoride for each gram of ferric sulfate).

Manganese. *Titration of Permanganate with an Equivalent Mixture of Nitrite and Arsenite:* Although permanganate can be titrated very easily with various reducing agents, e.g., with ferrous sulfate or iodometrically, the methods are not suitable when other oxidizing agents such as chromic acid or vanadic acid are present; the latter acid is usually found in solutions of steel after persulfate oxidation. Permanganate can be titrated with nitrite solution but the reaction is slow, especially near the end-point (cf. p. 69). Arsenite alone reduces permanganate to manganese (+3.3).[116] Titration with arsenite is a purely empirical method and has been applied by Bright and Larrabee[116] to the determination of manganese in steels. The method is used extensively in England in steelworks laboratories for the rapid routine determination of manganese.[117]

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[115] Z. G. Szabó and L. Csányi, *Anal. Chem.*, 21, 1144 (1949).

Sandell, Kolthoff, and Lingane[118] discovered particular conditions in which permanganate is reduced to manganese(II) in an acid solution by a mixture of nitrite and arsenite. The color change at the end-point is from violet to yellow-brown and can be seen very clearly with a little experience. They also found that the end-point of the titration was much sharper with a mixture of nitrite and arsenite than with either alone. The reaction is practically stoichiometric according to the equations

$$2MnO_4^- + 5As^{3+} + 16H^+ \longrightarrow 2Mn^{2+} + 5As^{5+} + 8H_2O$$

$$2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$$

although these authors recommended that the reagent mixture be standardized under the reaction conditions.

Reagent Solution: Dissolve 2.5 g. of pure arsenious trioxide in 25 ml. of 4*N* sodium hydroxide and dilute to 200 ml. with water. Neutralize the solution with a slight excess of dilute sulfuric acid and add a slight excess of sodium carbonate (pH 7–8). Add 0.85 g. of sodium nitrite and dilute to 1 liter. (After 1 year the titer of the solution had decreased by only 1.5 per cent when kept in the dark.)

Standardization (for the determination of manganese in steel): Pipette 10 ml. of 0.05*N* permanganate solution into a 250 ml. Erlenmeyer flask and add 1.0 g. of electrolytic iron of known manganese content and 30 ml. of acid mixture (100 ml. of concentrated sulfuric acid, 125 ml. of 85 per cent phosphoric acid, 250 ml. of nitric acid (d. 1.42)), and 525 ml. of water.[116] Warm the mixture until the iron is dissolved and finally boil for 2–3 minutes to remove nitrogen oxides. Add 50 ml. of cold water, 5 ml. of 0.1*N* silver nitrate, and 10 ml. of 30 per cent ammonium persulfate solution. Boil for 30–45 seconds and cool immediately to 20–25°C. in cold water. Add 5 ml. of 0.2*N* sodium chloride and 10 ml. of 12*N* sulfuric acid and titrate the permanganate with the reagent solution. Add the titrant at a steady rate of 5-6 ml. per minute while shaking strongly until the solution becomes pale pink. Then titrate slowly (1 drop per 5 seconds) and finally at 1 drop per 10 seconds. The end-point is reached when the color changes to white (suspension of silver chloride). If the titration is carried out properly, a drop of 0.05*N* permanganate added after the end-point should cause a red color lasting for at least 3 minutes; the end-point is exact to 0.02 ml. In the calculation of the result for manganese in steel a suitable correction is made.

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[116] Cf. H. A. Bright and C. P. Larrabee, *Bur. Standards J. Research*, **3**, 573 (1929); (a review of the older literature is given in this paper).

[117] *Standard Methods of Analysis of Iron, Steel and Ferro-alloys*, United Steel Co. Ltd., Sheffield, 1951.

[118] E. B. Sandell, I. M. Kolthoff, and J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **7**, 256 (1935).

Manganese in Steels: Weigh out 0.9–1.1 g. of the steel and dissolve in 30 ml. of the acid mixture. Treat further as above.

Notes: (1) The results are accurate to 0.01 per cent if the reagent solution is standardized under exactly the same conditions as in the actual determination.

(2) The silver which is present as catalyst must be removed with sodium chloride because the silver ion interferes in the titration.

(3) Chromic and vanadic acids have no influence on the titration.

Manganese. *Arsenite Method:* Hillson[119] determined large amounts of manganese (in ores or ferric manganese) by titrating the permanganic acid, formed by persulfate oxidation, with arsenite in the presence of osmic acid catalyst (cf. Gleu, p. 44).

Procedure: Dissolve the sample (30–50 mg. of manganese) in aqua regia. Filter and fuse the residue in a platinum crucible with sodium carbonate. If it is green, manganese is present; it should be dissolved and added to the filtrate. Add 18 ml. of concentrated sulfuric acid and evaporate to fumes. Transfer to a 250 ml. graduated flask and dilute to the mark with water. To a 25 ml. aliquot add 3–5 g. of disodium hydrogen phosphate, 10 ml. of phosphoric acid, 10 ml. of fresh 20 per cent ammonium persulfate solution, and 5 ml. of 0.1*N* silver nitrate. Boil for 2 minutes over a flame, cool quickly, and add 25 ml. of 6*N* sulfuric acid and some drops of osmic acid catalyst (1 g. in 390 ml. of 0.1*N* sulfuric acid). Run in an excess of 0.1*N* arsenite solution and back-titrate with permanganate in the presence of diphenylaminesulfonic acid, or titrate directly with arsenite in the presence of *o*-phenanthroline as indicator.

HYDRAZINES

Hydrazine has been used for the titration of several oxidizing agents.[120] It has no advantage over more conventional titrants and little need be said concerning its use. Meyer[121] determined *various aldehydes* by titrating with phenylhydrazine; he used G-orange or chromazone red N as external indicators.[122]

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[119] H. D. Hillson, *Ind. Eng. Chem., Anal. Ed.*, 16, 560 (1944).

[120] J. Zýka and J. Vulterin, *Collection Czech Chem. Communs.*, 20, 804 (1955); L. Erdey and I. Buzás, *Acta Chim. Acad. Sci. Hung.*, 6, 127 (1955); cf. E. de Metz, *Chem. Weekblad*, 21, 91 (1924) (a review of earlier literature is given in this paper).

[121] R. Meyer, *Z. anal. Chem.*, 140, 184 (1953).

Procedure: Dissolve about 2 g. of dichlorobenzaldehyde in about 50 ml. of glacial acetic acid contained in a 200 ml. beaker. Add 20 ml. of saturated sodium acetate solution. Titrate with 0.2N phenylhydrazine hydrochloride until a spot placed on the indicator paper gives a slight violet color (filter paper soaked in a 1 per cent aqueous solution of the indicator). An excess of 0.2 ml. of titrant can be readily observed.

Note: (1) With aldehydes which react slowly add an excess of titrant, set aside for 15–30 minutes, and back-titrate with 0.2N benzaldehydesulfonic acid.

(2) Nitrophenylhydrazine sulfonic acid is determined as follows:

Procedure: Dissolve 2–3 g. in 15–20 ml. of water, add 30 ml. of concentrated hydrochloric acid and a known excess of solid benzaldehydesulfonic acid (about 2 g.). Stir for 1 hour at 40°C. After hydrolysis and condensation have taken place, cool to room temperature, neutralize with sodium acetate, and titrate the unreacted benzaldehydesulfonic acid with 0.2N phenylhydrazine hydrochloride.

POTASSIUM FERROCYANIDE

The use of potassium ferrocyanide for the titration of zinc has already been considered in Vol. II, p. 301. The titration is actually a precipitation reaction, but the detection of the end-point is based on a redox reaction and further notes are made here for the sake of completeness.

A new range of redox indicators has been proposed for this titration by Belcher and coworkers. These indicators are naphthidine,[123] 3,3 -dimethylnaphthidine,[124] naphthidinesulfonic acid, and 3,3′-dimethylnaphthidinedisulfonic acid.[125] Of these, the best are undoubtedly the dimethyl derivatives. When the back-titration procedure described by Kolthoff and Pearson[126] (who used diphenylamine or diphenylbenzidine as indicator) was followed, excellent end-points were obtained even with 0.001M solutions. The indicators have also been used in the titration of cadmium with ferrocyanide;[127] excellent end-points are obtained using a direct titration. Similar procedures have been developed for the titration of indium,[127] gallium,[128] and calcium.[127] The titration of calcium is not so satisfactory as those of the other elements because of the solubility of calcium ferrocyanide. The titration must be carried out in 70–80 per cent ethanol. In all applications of these indicators the end-point color changes are considerably better than those using *o*-dianisidine or diphenylbenzidine.

Indicator Solutions: Dissolve 0.2 g. of 3,3′-dimethylnaphthidine in 100 ml. of glacial acetic acid by warming. Alternatively dissolve 0.2 g. of 3,3′-dimethyl-naphthidinesulfonic acid in a slight excess of ammonia and boil out the excess. Dilute the solution to 100 ml. with water.

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[122] Cf. F. Feigl, V. Anger, and R. Zappert, *Mikrochemie*, 15, 190 (1934).

[123] R. Belcher and A. J. Nutten, *J. Chem. Soc.*, 1951, 548.

[124] R. Belcher, A. J. Nutten, and W. I. Stephen, *ibid.*, 1951, 1520.

[125] *Idem, ibid.*, 1952, 1269, 3857.

[126] I. M. Kolthoff and E. A. Pearson, *Ind. Eng. Chem., Anal. Ed.*, 4, 147 (1932).

[127] R. Belcher, A. J. Nutten, and W. I. Stephen, *J. Chem. Soc.*, 1951, 3444.

[128] R. Belcher, A. J. Nutten, and W. I. Stephen, *J. Chem. Soc.*, 1952, 2438.

Procedure. Zinc: To about 20 ml. of the zinc solution add sufficient sulfuric acid to give a final acidity of $1N$ and 10 ml. of 10 per cent ammonium sulfate and dilute the solution to 50 ml. with water. Add 4 drops of 1 per cent potassium ferricyanide solution and 2 drops of indicator and titrate with $0.05M$ potassium ferrocyanide until the color changes from purple-red to green. Add a 10–20 per cent excess of the titrant and then back-titrate with a standard zinc solution.

Notes: (1) With $0.005M$ solutions, the final concentrations of sulfuric acid and ammonium sulfate should be $0.2N$ and 0.4 per cent, respectively; with $0.001M$ solutions, the concentrations should be $0.1N$ and 0.2 per cent, respectively. Correspondingly dilute solutions of the indicators should be used.

(2) With the free base as indicator, the initial color change is slow owing to adsorption of the oxidized indicator on the precipitate of zinc ferrocyanide. When a slight excess of ferrocyanide is present, desorption is rapid and the precipitate changes to a grey-green color. With the disulfonic acid the color change is instantaneous.

Cadmium: To the neutral cadmium solution, add 10 ml. of 10 per cent ammonium sulfate solution and dilute to 40 ml. Add 2 drops of 1 per cent potassium ferricyanide and 2 drops of indicator and titrate with $0.01M$ or $0.05M$ potassium ferrocyanide until the color changes from red-violet to white.

Notes: (1) A back-titration method can also be applied.

(2) Both the free base and the disulfonic acid indicators give instantaneous color changes.

(3) The precipitate has the formula $Cd_5K_6(Fe(CN)_6)_4$, indicating a 5:4 relationship between cadmium and ferrocyanide.

SODIUM NITRITE

Sulfamates: Bowler and Arnold[129] determined sulfamates by direct titration with nitrite:

$$NO_2^- + NH_2SO_2OH \longrightarrow N_2 + HSO_4^- + H_2O$$

Procedure: To 100 ml. of solution containing 0.15–0.2 g. of sulfamic acid add 10 ml. of 10 per cent sulfuric acid and titrate slowly at room temperature into an Erlenmeyer or iodine flask with $0.2N$ nitrite solution. After each 5 or 10 ml. addition of titrant, stopper the flask and shake vigorously to remove nitrogen. Near the end-point titrate dropwise and shake after each addition. Use starch-iodide solution as an external indicator.

Notes: (1) Naphthol blue black, which may also be added, changes from blue to purple near the end-point. It is not satisfactory for the exact determination of the end-point but is useful for giving a preliminary warning.

(2) In the presence of interfering oxidants, Griess' diazo reagent can be used in place of starch-iodide for detection of the end-point.

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[129] W. W. Bowler and E. A. Arnold, *Anal. Chem.*, 19, 336 (1947).

Azide: According to Reith[130] azide can be titrated with sodium nitrite. The end-point is detected by placing a drop of the solution on a spotplate and adding 5 drops of sulfuric acid, starch, and 2 mg. of potassium iodide; at the end-point a blue color appears. Ferric iron may be used as an internal indicator. Ferric azide has a blood-red color which is bleached by much mineral acid, but some should be present otherwise the reaction is slow.

Procedure: Transfer 0.5 ml. of 5 per cent azide solution to a glass-stoppered reagent vessel and add 2 ml. of 10 per cent ferric chloride solution and 1 ml. of 4*N* sulfuric acid. Titrate with 0.1 per cent nitrite solution from a microburette to colorless. Make the addition slowly and with constant shaking and preferably use a comparison solution to detect the end-point.

Note: The indicator is very sensitive; in a mixture of 2 ml. of ferric chloride, 1 ml. of 4*N* sulfuric acid, and 5 ml. of water, even 0.03 mg. of N_3H gives a brown color.

Diazotization Reactions: Nitrite is generally used as a reagent in diazotization reactions:

$$RNH_2 + HX + HNO_2 \longrightarrow ArN_2X + 2H_2O$$

Determination of Amines: Phillips and Lowy[131] give the following method for the titration of aromatic amines.

Procedure: Dissolve a weighed amount of amine sample in 100 ml. of 1.2*N* hydrochloric acid in a glass-stoppered flask and add standard 0.1*N* nitrite solution dropwise at 20–23°C. until iodine starch paper is *immediately* colored blue. Close the flask and set aside, shaking occasionally for 15 minutes. If a drop of the solution then gives only a slight blue color or none at all, titrate back with 0.1*N* aniline chloride or 0.1*N* sulfanilic acid solution.[132] Usually there is about 2 ml. of nitrite solution in excess.

Notes: (1) As nitrous acid is unstable, it is necessary to run a blank determination with 2 ml. of nitrite solution in 100 ml. of 1.2*N* hydrochloric acid under the above conditions, and titrate with aniline chloride or sulfanilic acid solution. The nitrite lost is deducted from the amount found (about 0.2 ml. of nitrite is lost).

(2) In this way, it is possible to determine 2,4,6-triaminobenzoic acid, 2,4,6-triaminotoluene, 1,3,5-triaminobenzene, 2,4,6-triaminochlorobenzene, metanilic acid, *m*-phenylenediamine, *m*-toluylenediamine with an accuracy of 1 per cent. No satisfactory values could be obtained with 2,4,6-triaminophenol, 1,2,4-triaminobenzene, *o*-phenylenediamine, or *p*-phenylenediamine.

(3) The nitrite solution is standardized against aniline hydrochloride or sulfanilic acid solution.

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[130] H. F. Reith, Dissertation, Utrecht, 1929.

[131] J. Phillips and A. Lowy, *Ind. Eng. Chem., Anal. Ed.*, **9**, 381 (1937).

[132] Cf. Schultz and W. Vaubel, *Z. Farben-Ind.,* **1**, 37, 149, 339 (1902); cf. G. Lunge, *Chem. Ztg.*, **28**, 501 (1904); S. Ueno and H. Sekiguchi, *J. Soc. Chem. Ind. Japan,* **37**, 235 (1934).

Organic Sulfur Compounds: Calamari *et al.*[133] assayed various sulfa drugs by titration with nitrite.

Standardization Procedure: To 0.52 g. sulfanilamide dissolved in 7 ml. of concentrated hydrochloric acid add 35 ml. of water. Add 30 g. of ice and titrate with 0.1*M* nitrite. Use starch paste or paper as external indicator. One milliliter of 0.1*M* $NaNO_2$ corresponds to 0.01722 g. of sulfanilamide.

Notes: (1) Sulfanilamide is obtained in primary standard form by recrystallizing twice from acetone and once from water. The assay is done in exactly the same way as the standardization. Sulfapyridine, sulfathiazole, sulfaguanidine, and sulfadiazine were assayed in this way.

(2) Frost[134] prefers to use acriflavine as internal indicator. The color change is from yellow to violet and is irreversible. The indicator should be added only when the end-point is approached. If it is added earlier a further addition should be made near the end-point. Agren[135] used diphenylbenzidine violet as internal indicator in the titration of a similar range of compounds. A similar method may be used for the determination of aromatic sulfonic acids[136] and isoniazid.[137]

3. Organic Titrants. ***Hydroquinone as Reagent for Gold:*** Hydroquinone is a suitable reagent for the macro or micro titration of gold. Pollard[138] found that gold is quantitatively converted to the trivalent form by treatment with bromine and hydrochloric acid or aqua regia. The excess of bromine or chlorine is removed with a stream of air and the gold is titrated with hydroquinone, *o*-dianisidine serving as indicator.

$$2HAuCl_4 + 3C_6H_6O_2 \longrightarrow 2Au + 3C_6H_4O_2 + 8HCl$$

Standard Hydroquinone Solution: Dissolve 0.4186 g. of pure hydroquinone in 200 ml. of water and 10 ml. of hydrochloric acid and dilute with water to 500 ml. (1 ml. corresponds to 1 mg. of gold).

Standard Gold Solution: Dissolve 0.5 g. of pure gold in 2 ml. of nitric acid and 6 ml. of hydrochloric acid by gentle warming. Remove the dissolved gases with air and dilute to 500 ml.

o-Dianisidine Indicator: Dissolve 0.5 g. in 200 ml. of water and 2 ml. of hydrochloric acid and dilute to 500 ml.

Procedure: To the gold(III) solution add 2 drops of concentrated hydrochloric acid, potassium bifluoride as buffer, and 1 ml. of indicator. Titrate with the hydroquinone solution immediately until the red color of the indicator disappears.

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[133] J. A. Calamari, R. Hubata, and P. B. Roth, *Ind. Eng. Chem., Anal. Ed.,* 14, 534 (1942).

[134] H. F. Frost, *Analyst,* 68, 51 (1943).

[135] A. Agren, *Svensk Farm. Tidskr.,* 55, 229 (1951).

[136] S. Ponzini, *Chem. Abstr.,* 42, 3701 (1948).

[137] P. G. W. Scott, *J. Pharm. and Pharmacol.,* 4, 686 (1952).

[138] W. B. Pollard, *Analyst,* 62, 597 (1937); cf. *Trans. Inst. Mining and Metallurgy,* 41, 434 (1932); A. R. Jamieson and R. S. Watson, *Analyst,* 63, 702 (1938).

Notes: (1) Copper, silver, iron(III), nickel, zinc, cadmium, aluminum, and tin do not interfere in 10 mg. amounts. The interference of lead can be avoided by diluting the aqua regia solution and adding a little bromine water; the bromine is removed with air.

(2) The pH of the solution is important because in too acid solutions the reaction of chloroauric acid and *o*-dianisidine is slow; in too alkaline solutions, a precipitate is formed.

(3) The best results are obtained with less than 2 mg. of gold. If more is present, the indicator should be added near the end-point.

(4) Traces of gold can be quantitatively precipitated with tellurium from 1.5–5*N* hydrochloric acid solution by sulfur dioxide. The gold is then dissolved and determined as described above. Palladium is also carried down by tellurium and interferes in the titration; gold may be separated by precipitation with "metol" or *p*-phenylenediamine hydrochloride.

(5) Belcher and Nutten[139] preferred 3-methylbenzidine and 3,3′-diethylbenzidine as indicators; the respective color changes are green to pale violet and yellow-green to pale violet. One per cent solutions of the indicators in glacial acetic acid were used.

(6) Hydroquinone has recently been used as a titrant for the determination of several oxidants. The titrations were mainly carried out potentiometrically.[140]

Methylene Blue as Reagent for Stannous Tin: Leutwein[141] titrates stannous tin in 4–6*N* hydrochloric acid under an atmosphere of carbon dioxide with a standard solution of methylene blue until a blue color appears. Stannic tin can be reduced with aluminum wire. Most other reductors do not give good results because they interfere with the titration. Large amounts of iron should be absent. Detailed procedures are given for the determination of tin in ores and alloys. The method is, however, of limited applicability and reference should be made to the original paper.

Methyl Orange as Reagent for Hypochlorite: Traces of hypochlorite can be determined in the presence of chloramine by titration with 0.02 per cent methyl orange in a medium 0.01*N* in hydrochloric acid.[142] It is essential to use methyl orange of high purity; otherwise irregular results are obtained. A linear relationship is then obtained according to the reaction:

$$(CH_3)_2NC_6H_4N{=}NC_6H_4SO_3Na + 2Cl_2 \longrightarrow (CH_3)_2NC_6H_4NCl_2 + Cl_2NC_6H_4SO_3Na$$

4. Redox Titrations in Nonaqueous Media. Titrations in nonaqueous media have hitherto been confined to neutralization reactions and the technique is now well-established as a useful and versatile analytical tool. Very little consideration had been given to the

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[139] R. Belcher and A. J. Nutten, *J. Chem. Soc.*, 1951, 551.

[140] V. Simon and J. Zýka, *Chem. Listy*, 49, 1646 (1955); *Collection Czech Chem. Communs.*, 21, 571 (1956).

[141] F. Leutwein, *Z. anal. Chem.*, 120, 233 (1940).

[142] E. L. Molt, *Chem. Weekblad*, 52, 265 (1956).

Table I

Substance titrated	Titrant Br_2	CrO_3	$NaMnO_4$	$TiCl_3$
As(III)	Deviation *ca.* 1%	Titration not possible	—	—
Sb(III)	Deviation >1%	Sb titrated in presence of As; max. devn. 3%	—	—
Hg(I)	Deviation *ca.* 3%	Poor results	—	Large errors
Se(IV)	Titration possible; results poor	—	—	—
Fe(II)	Deviation *ca.* 3%	Deviation *ca.* 5%	Deviation *ca.* 3%	—
Fe(III)	—	—	—	Deviation 0.5%
Tl(I)	Deviations 1–2%	—	—	—
I^-	Not quantitative	Poor	—	—
H_2O_2	—	Satisfactory	—	—
Dihydric phenols	Satisfactory	Satisfactory	Satisfactory	—
Aminophenols	Unsatisfactory	Unsatisfactory	Unsatisfactory	—
Diphenylamine	Unsatisfactory	Deviation >0.5%	—	—

possibility of carrying out other reactions in nonaqueous media until Tomíček and his coworkers[143] described investigations in which they had studied several redox processes in glacial acetic acid medium and the determination of halides by titration with lead and mercuric salts. This type of titration is not yet fully developed and any advantages it may have are not yet evident, but a brief account of the work will give an idea of the possible uses (cf. p. 158).

Tomíček and Heyrovský[143] prepared bromine, chromic acid, sodium permanganate, and titanous chloride solutions in glacial acetic acid which they used to titrate several inorganic and organic substances: a potentiometric method was used to detect the end-point. Their findings are summarized in Table I.

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[143] O. Tomíček and A. Heyrovský, *Collection Czech Chem. Communs.*, **15**, 997 (1950); *Chem. Listy*, **44**, 245 (1950); O. Tomíček and J. Valcha, *Collection Czech Chem. Communs.*, **16–17**, 113 (1951–52); *Chem. Listy*, **44**, 283 (1950); O. Tomíček, *ibid.*, **47**, 516 (1953); *Chem. Abstr.*, 49, 15602 (1955).

Tomíček and Valcha[143] continued these studies and also examined the use of bromine, iodine, iodine monobromide, iodine monochloride, and lead tetraacetate as titrants. Aniline, *N*-dimethylaniline, ascorbic acid, and hydroquinone were titrated satisfactorily with bromine. Iodine was unsatisfactory as a titrant because of its low reactivity. Iodine monobromide was also unsuitable but iodine monochloride gave good results with some compounds (hydroquinone, oleic acid, resorcinol, and antipyrine). Lead tetraacetate also proved suitable for the titration of several organic compounds (hydroquinone, tetrachlorohydroquinone, catechol, and ascorbic acid); it was unsatisfactory for the direct titration of glycols and mandelic acid but it was possible to add an excess of lead tetraacetate and then to back-titrate with hydroquinone. These titrations were also done potentiometrically, but some visual indicators have also been described. Quinalizarin was satisfactory for titrations with lead tetraacetate; the use of alizarin blue was also mentioned, but no details of its use have so far been described. There is clearly a field for the development of other suitable indicators.

An assessment of the value of this new technique must await the publication of further studies and applications.

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SUBJECT INDEX

Methods are generally indexed according to the first standard solution which is used. Page numbers where more detailed information is given are shown in heavy type. The following symbols are used.

As = *arsenite method*
Br = *bromate or bromine method*
Ce = *cerimetric method*
Cr = *dichromate method*
Fe = *ferrous iron method*
I = *iodometric method*
In = *indicator*
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R = *reagent used as standard solution*
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